

| REPORT DOCUMENTATION PAGE | | | Form Approved OMB No. 0704-0188 | |
|--|---|---|------------------------------------|--|
| <small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small> | | | | |
| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE February 20, 1995 | 3. REPORT TYPE AND DATES COVERED Final Report-July 21, 1994-January 21, 1995 | | |
| 4. TITLE AND SUBTITLE Epitaxial Growth of High Quality SiC of Pulsed Laser Deposition | | 5. FUNDING NUMBERS F33615-94-C-5417 | | |
| 6. AUTHOR(S) David G. Hamblen, David B. Fenner Peter A. Rosenthal, Joseph Cosgrove, Pang-Jen Kung | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Advanced Fuel Research, Inc. 87 Church Street P.O. Box 380379 East Hartford, CT 06138-0379 | | 8. PERFORMING ORGANIZATION REPORT NUMBER 526033 | | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dept. of the Air Force Air Force Material Command (ASC) Wright Laboratory (WL/MLKN) Wright-Patterson AFB, OH 45433-6503 | | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER 0001AF | | |
| 11. SUPPLEMENTARY NOTES | | | | |
| 12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public release: SBIR Report, distribution unlimited | | 12b. DISTRIBUTION CODE 19950227 071 | | |
| 13. ABSTRACT (Maximum 200 words) The goal of this research program is to develop Pulsed Laser Deposition (PLD) as a method for depositing device quality, single crystal silicon carbide (SiC) thin films. Phase I has demonstrated the ability to deposit single crystal 3C-SiC thin films on Si (100) and 6H-SiC (0001) substrates. An existing PLD facility was improved for SiC depositions. Prior to PLD, all substrates were prepared using a novel spin etch technique. Numerous experiments explored the effect of substrate temperature and laser fluence on the resulting SiC films. Composition of the films was measured by Rutherford backscattering spectrometry and Scanning Auger Microprobe. The films were slightly carbon-rich although the excess carbon component was attributed to background contaminants in our vacuum system. Optical analyses included Fourier Transform infrared (FT-IR) spectroscopy. Epitaxy of the 3C-SiC films was confirmed by x-ray diffraction, transmission electron microscopy, and electron diffraction. Epitaxial SiC films were grown on Si (100) at temperatures as low as 930° C, although the crystallinity of the films improved with increasing temperature. The best films result at laser fluences of 1.5 - 2 J/cm ² . Single crystal films were obtained on 6H-SiC (0001) and vicinal 6H-SiC (0001) oriented 3.5 towards [1120] at 1200° C. | | | | |
| 14. SUBJECT TERMS Pulsed Laser Deposition, Spin Etch, SiC, Epitaxial | | 15. NUMBER OF PAGES 42 | | |
| | | 16. PRICE CODE | | |
| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT | |

**"EPITAXIAL GROWTH OF HIGH QUALITY SIC OF
PULSED LASER DEPOSITION"**

**- Phase I -
Final Report**

For the Period
July 21, 1994 - January 21, 1995

Sponsored by
Department of Defense/Air Force
Wright-Patterson Laboratory, Wright-Patterson AFB, OH
Small Business Innovation Research Program

Contract Number: F33615-94-C-5417

Prepared by:
David G. Hamblen
David B. Fenner
Peter A. Rosenthal
Joseph Cosgrove
Pang-Jen Kung

of

Advanced Fuel Research, Inc.
87 Church Street
East Hartford, CT 06108

February 3, 1995

| | |
|----------------------|---|
| Accession For | |
| NTIS | CRA&I <input checked="" type="checkbox"/> |
| DTIC | TAB <input type="checkbox"/> |
| Unannounced | <input type="checkbox"/> |
| Justification _____ | |
| By _____ | |
| Distribution / _____ | |
| Availability Codes | |
| Dist | Avail and/or Special |
| A-1 | |

This material is based on work supported by the Department of Defense under Contract No. F33615-94-C-5417. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the Department of Defense.

**"EPITAXIAL GROWTH OF HIGH QUALITY SiC OF
PULSED LASER DEPOSITION"**

Table of Contents

| | | |
|-----|---|----|
| 1.) | Project Summary | 1 |
| 2.) | Introduction | 2 |
| | 2.a. Identification and Significance of the Problem or Opportunity..... | 2 |
| | 2.b. The Innovation..... | 2 |
| | 2.c. Phase I Technical Objectives..... | 3 |
| | 2.d. Summary of Phase I Accomplishments..... | 3 |
| | 2.e. Technical Background | 4 |
| | 2.e.1. SiC Thin Film Progress..... | 4 |
| | 2.e.2 Pulsed Laser Deposition..... | 5 |
| 3.) | Technical Results..... | 7 |
| | 3.a. Task 1 - Assemble Apparatus..... | 7 |
| | 3.b. Task 2 - Prepare Substrates | 9 |
| | 3.c. Task 3 - Deposit Thin Films of 3C-SiC on 6H-SiC and Si..... | 11 |
| | 3.d. Task 4 - Analysis of SiC Films..... | 12 |
| 4.) | Conclusions and Recommendations..... | 39 |
| | Acknowledgments..... | 40 |
| | References | 41 |

"EPITAXIAL GROWTH OF HIGH QUALITY SiC OF PULSED LASER DEPOSITION"

1. Project Summary

The goal of this research program is to develop Pulsed Laser Deposition (PLD) as a method for depositing device quality, single crystal silicon carbide (SiC) thin films. Phase I has demonstrated the ability to deposit single crystal 3C-SiC thin films on Si (100) and 6H-SiC (0001) substrates. An existing PLD facility was improved for SiC depositions. Prior to PLD, all substrates were prepared using a novel spin etch technique. Numerous experiments explored the effect of substrate temperature and laser fluence on the resulting SiC films. Composition of the films was measured by Rutherford backscattering spectrometry and Scanning Auger Microprobe. The films were slightly carbon-rich although the excess carbon component was attributed to background contaminants in our vacuum system. Optical analyses included Fourier Transform infrared (FT-IR) spectroscopy. Epitaxy of the 3C-SiC films was confirmed by x-ray diffraction, transmission electron microscopy, and electron diffraction. Epitaxial SiC films were grown on Si (100) at temperatures as low as 930° C, although the crystallinity of the films improved with increasing temperature. The best films result at laser fluences of 1.5 - 2 J/cm². Single crystal films were obtained on 6H-SiC (0001) and vicinal 6H-SiC (0001) oriented 3.5 towards [11 $\bar{2}$ 0] at 1200° C.

Potential Applications The potential applications for high quality SiC thin film devices are numerous. Its superior properties make SiC an attractive choice for high temperature, high frequency and high power electronic applications. SiC is an ideal candidate for sensors in high temperature operations such as jet and automobile engine environments. The development of a high temperature and high speed thin film semiconducting material will greatly stimulate new commercial applications in communications and high speed computing. The PLD method is ideal due to its flexibility and low cost.

2. Introduction

2.a. Identification and Significance of the Problem or Opportunity

The attractiveness of SiC as an advanced semiconducting material derives from its many superior properties such as high breakdown voltage, high saturated electron drift velocity, high thermal conductivity and resistance to high temperature effects. SiC is capable of both n- and p-type conductivity and can be oxidized to form electrically insulating SiO₂ (1). As a result of these properties, SiC is a leading candidate for high temperature, high frequency and high power electronic applications (2). Two polytypes of SiC which have received the most attention are the 3C cubic structure (β -SiC) and the 6H hexagonal structure due to their individual properties of higher electron mobility (1000 cm²/V•s) and larger band gap (2.9 eV), respectively (1).

Continued improvements in the quality of SiC thin films are imperative for the development of SiC device technology. Thin film growth of 3C-SiC on Si substrates has been motivated by the availability of low-cost, large diameter, high purity Si substrates and the need for SiC/Si heterojunction devices. Films grown on Si are particularly high in defect density owing to the large lattice and thermal expansion mismatches between 3C-SiC and Si (3,4,5). While buffer methods exist that alleviate the lattice mismatch problem, resolving the thermal expansion mismatch requires lower deposition temperatures than those employed by conventional CVD (1200 - 1400° C). Significant improvements in SiC thin film epitaxy are obtained when grown on 6H-SiC substrates. Both the 3C and 6H-SiC polytypes are obtained, although stacking faults and double positioning boundaries (in the 3C polytype) are still a problem (6). Recent studies indicate that the resulting polytype of SiC grown on 6H-SiC is dependent not only on substrate orientation (on-or off-axis) but also on substrate temperature, while variations in substrate pretreatment can affect the defect density in 3C-SiC films grown on 6H-SiC. From these observations, it is clear that a deposition process which provides precise control of SiC thin film growth on 6H-SiC and Si substrates is required for the production of device-quality SiC thin films.

2.b. The Innovation

The solution offered by this proposal was the development of a process for the growth of high quality, single crystal SiC films using Pulsed Laser Deposition (PLD). PLD enjoys several advantages over other deposition techniques that make it an attractive choice for depositing advanced material thin film structures. PLD is widely regarded as a controlled, layer by layer technique with an inherent ability to maintain the target stoichiometry in the deposited film. PLD can easily deposit multi-layer thin film structures, including multi-element materials. The highly energetic growth flux generated by PLD can potentially lower growth temperature, and improve overall film structure.

The elimination of contamination (hydrocarbon, oxygen) is important for epitaxial growth of 3C-SiC on Si. Fortunately, scientists now at Advanced Fuel Research, Inc. (AFR) have developed a unique spin etch method for cleaning silicon (7,8) that reduces carbon and oxygen contaminations to < 0.05 monolayer and passivates the surface until deposition begins. The technique is so successful that high-temperature superconducting YBaCuO films deposited on spin etched Si have a much higher critical current density than films deposited on conventionally cleaned Si (9,10). Furthermore, preliminary research at AFR has demonstrated the deposition of epitaxial 3C-SiC on spin etched Si at substrate temperatures of 900 - 950° C using PLD (11,12). Because of the success of the spin etch technique on Si substrates, and the chemical similarities between the oxidized surfaces of Si (111) and the Si face of 6H-SiC (0001), the spin-etch technique should be adaptable to 6H-SiC substrates.

AFR is in a unique position to develop Pulsed Laser Deposition as a technique for producing high quality SiC on 6H-SiC and Si substrates.

2.c. Phase I Technical Objectives

The overall goal of the Phase I research was to deposit high quality, epitaxial SiC thin films on 6H-SiC and Si substrates. The specific objectives of this research were:

- **Task 1 - Assemble Apparatus** - Modify the existing apparatus to enable the control of all important experimental parameters.
- **Task 2 - Prepare Substrates** - Obtain substrates of various orientations of the 6H-SiC and Si and prepare for deposition by the spin etch method.
- **Task 3 - Deposit Thin Films of SiC on 6H-SiC and Si** - Deposit thin films of 6H-SiC and 3C-SiC on 6H-SiC substrates and 3C-SiC on Si substrates using Pulsed Laser Deposition. Adjust deposition parameters to optimize film quality and lower Si substrate temperature.
- **Task 4 - Analysis of SiC Films** - Apply a variety of structural, compositional, and electrical analyses to determine the quality of the deposited films. Perform analyses continuously as feedback to guide experimental parameters.

2.d. Summary of Phase I Accomplishments

The Phase I program has demonstrated that epitaxial growth of single crystal 3C-SiC on Si and 6H-SiC substrates can be achieved by PLD. The specific accomplishments of this program can be summarized as follows:

- Improved a PLD facility for depositing SiC thin films on single crystal Si and 6H-SiC substrates.
- Demonstrated the deposition of SiC films with no evidence of particulate contamination.
- Investigated the effects of laser fluence and growth temperature on the quality of the SiC films.
- Characterized the SiC films with an array of analyses, including x-ray diffraction, transmission electron microscopy, electron diffraction, Rutherford backscattering spectroscopy and FT-IR spectroscopy.
- Demonstrated epitaxial growth of 3C-SiC on Si substrates at relatively low temperatures.
- Demonstrated epitaxial growth of 3C-SiC on 6H-SiC substrates.
- Developed a theoretical model for the infrared reflectance of SiC that includes effects of doping and film thickness. Excellent agreement was obtained between theory and experiment, using the films made in this program.

2.e. Technical Background

The background for this proposal is in two areas: 1) SiC thin film progress, and 2) Pulsed Laser Deposition.

2.e.1. SiC Thin Film Progress

Silicon carbide is a wide band gap semiconducting material which is praised for its many superior properties such as high breakdown voltage, high saturation drift velocity, high thermal conductivity and resistance to high temperature effects. SiC is capable of both n- and p-type conductivity and can be oxidized to form electrically insulating SiO_2 (1). As a result of these properties, SiC is a leading candidate for high temperature, high frequency and high power applications.

SiC exhibits a special type of one-dimensional polymorphism known as polytypism. SiC polytypes differ from each other in the stacking sequence of the tetrahedrally bonded SiC bi-layers. Each bi-layer can exist in one of three positions with respect to the crystal lattice. Each position is designated as either A, B, or C. The two polytypes which have received the most attention are the zinc-blend (cubic) structure, designated as 3C-SiC (ABC . . . stacking sequence) and the hexagonal 6H-SiC (ABCACB . . . stacking sequence) structure. Interest in 3C-SiC derives from its high electron mobility ($1000 \text{ cm}^2/\text{V} \cdot \text{s}$) while 6H-SiC is envisioned for blue LEDs because of its wide band gap (2.8 eV). Unfortunately, it is difficult to grow purely single-phase SiC (6). The relative ease with which polytypism occurs results in stacking fault defects which ultimately can degrade the material's electronic properties. Propagation of various polytypes can result from thermal fluctuations, impurities and deviations from stoichiometry, and may also depend on growth rate (2).

Much research has been devoted to the growth of 3C-SiC on Si substrates due to the availability of low-cost, large diameter, high purity Si and the desire for SiC/Si heterojunction devices. Heteroepitaxy of 3C-SiC on Si is typically achieved by Chemical Vapor Deposition (CVD). CVD of 3C-SiC on Si usually involves a processing sequence similar to the following: 1) a high temperature etch of the substrate at 1200°C in dilute HCl gas to remove the native surface oxide, 2) the formation of a thin buffer layer by carburizing the Si using a hydrocarbon (typically propane) in H_2 at $1300 - 1400^\circ \text{C}$, thereby relieving the relatively large lattice mismatch ($\sim 20\%$) (13), and 3) CVD of the 3C-SiC film using silane and a hydrocarbon in H_2 (13,14). A major goal of SiC growth on Si has been to lower the deposition temperature in order to reduce defects induced by the thermal expansion mismatch between the SiC film and the Si ($\sim 8\%$). The lowest epitaxial growth temperatures to date have been achieved by Golecki et al (3). Single crystal 3C-SiC on Si (100) was obtained as low as 750°C using low pressure CVD of SiCH_3H_3 in H_2 . The XRD rocking curves are comparable to conventional CVD SiC films on Si. The authors attribute their success to the use of a single gaseous precursor which avoids deviations from stoichiometry. Wahab et al. (15) has also demonstrated low temperature epitaxial growth by Reactive Magnetron Sputtering (RMS). Unfortunately, 3C-SiC films grown on Si are still plagued by defects including stacking faults, microtwins, and misfit dislocations. Despite the defects, these films have significantly contributed to the development of the present doping technology for SiC films (2).

Improvements in the quality of SiC thin films have resulted when grown on single crystal 6H-SiC substrates by CVD. 3C-SiC (111) films grown on the non-vicinal Si (0001) and C (0001) faces of 6H-SiC at $1400 - 1550^\circ \text{C}$ by Davis et al. (2) reveal few defects when analyzed by cross-sectional transmission electron microscopy (TEM), however, plan-view TEM indicates the presence of double positioning boundaries (DPB) accompanied by stacking faults. Nucleation can occur at either one of two equivalent

sites, which results in either the ABCABC . . . or ACBACB . . . stacking sequence of the 3C-SiC (2). Neighboring islands of the two different stacking sequences will be rotated 60° relative to each other and upon coalescence, DPBs will form. Elimination of the DPBs was achieved by growing films on vicinal 6H-SiC (0001) oriented 3° towards $[11\bar{2}0]$ at 1500° C (2,16). The resulting polytype is 6H-SiC and few defects are present. Stan et al. (17) have demonstrated that SiC films deposited on the C face of a 6H-SiC (0001) substrate at ~1200° C by PLD were the 2H polytype. The authors utilized a KrF excimer laser (248 nm) pulsed at 2 Hz. In contrast, Rowland et al. (18) demonstrated that SiC films grown by Gas-Source Molecular Beam Epitaxy (GSMBE) at 1050 - 1250° C on vicinal 6H-SiC (0001) oriented 3 - 4° towards $[11\bar{2}0]$ were the 3C polytype. The films were single crystal, but contained DPBs. DPB-free films of 3C-SiC films have been obtained by GSMBE on 6H-SiC (0114) substrates (19). Most recently, reductions in DPB density have been demonstrated on 15R-SiC substrates (20,21). These examples illustrate the complex dependence of the SiC film polytype and defect density on various parameters, including temperature, substrate, and deposition technique.

2.e.2. Pulsed Laser Deposition

In PLD, a pulsed laser beam is focused onto a target, resulting in a highly energetic plasma (plume) of neutrals and ions which are directed onto a substrate. The intense pulsed energy density at the target is the driving force for effectively depositing materials containing elements with different vapor pressures. Typically, an excimer (or a harmonic of Nd:YAG) laser is pulsed onto a target at a rate of 1 - 10 Hz, yielding a deposition rate of 1 to 20 Å/sec. In practice, the pulsed laser beam is "rastered" across the target surface, to avoid gross morphological changes of the target and the potential of "plume tilting" away from the substrate. The following is a list of several advantages that make PLD an attractive method for depositing many advanced material thin films:

- ⇒ With the correct process parameters, PLD is a controlled technique with an inherent ability to maintain the target stoichiometry in the deposited film. Deviations from stoichiometry can lead to defects such as antisite defects, which would degrade the electronic properties of the film (22), or result in the wrong phase, making the film completely unsuitable.
- ⇒ By virtue of its versatility and relative simplicity, PLD is a convenient technique for depositing multi-layer thin film structures, in-situ, by utilizing a movable, multi-target holder.
- ⇒ The high energies associated with the plume species enhance surface diffusion and thus can potentially lower growth temperature while improving film adhesion and structure. Donley and Zabinski (23) note improved adhesion of tribological coatings grown by PLD. They attribute their findings to improved density, stoichiometry and crystalline structure of the films.
- ⇒ PLD can be performed at pressures $< 10^{-4}$ Torr as we have demonstrated in the case for SiC. At these pressures, in-situ RHEED diagnostics can be employed. Valuable structural information regarding the film can thus be obtained during the growth process. This is a clear advantage over conventional Chemical Vapor Deposition (CVD) and Sputtering techniques, which typically operate above 10^{-4} Torr.
- ⇒ The cost of set-up and operation of PLD is relatively inexpensive. The cost of a comparable Molecular Beam Epitaxy (MBE) system or Metal-Organic CVD system are about an order of magnitude higher.

⇒ An extremely wide range of materials can be deposited by PLD, and many elements simultaneously, which is very difficult by MBE and CVD.

While the aforementioned advantages would enable PLD to be a leading manufacturing process for electron thin films, some hurdles do remain. Traditionally, PLD progress has been slowed by 1) the co-deposition of particles with the thin film, and 2) the relatively small deposition area. The former problem will have serious consequences on the electronic properties of thin film devices, however, proper adjustment of process parameters can avoid high density particle deposition. In general, the size and density of particles increases with increasing laser wavelength, and increasing laser fluence (24). Furthermore, the use of high density targets minimizes particle contamination. At AFR, YBaCuO films grown on YSZ (yttria stabilized zirconia) buffered Si (100) exhibit superior superconducting properties and are essentially particle free. The films are deposited with a Nd:YAG laser at 266 nm focused onto a highly dense (95%) YBaCuO target. The fluence at the target is estimated to be 1.5 - 2 J/cm².

Recent progress has resulted in the ability to cover large diameter substrates. Innovative techniques such as "Off-Set" (OS) PLD, "Rotational/Translationals" (R/T) PLD, and "Rastering" PLD have demonstrated coverage of 50 - 100 mm diameter substrates (25,26). The Rastering approach is especially promising in that good, uniform coverage has recently been demonstrated on substrates as large as 150 mm in diameter (26). It should be noted that large area deposition of SiC on SiC substrates is currently limited by the available size of single crystal SiC substrates. 30 mm SiC substrates are now in production, with a very limited availability of 50 mm substrates. Our PLD system can easily be adapted to 30 mm substrates.

3. Technical Results

3.a. Task 1 - Assemble Apparatus

Objective

Modify the existing apparatus to enable control of all the important experimental parameters.

Results

An existing PLD facility was utilized for all SiC thin film depositions. The system, shown in Figure 1 is based on a Continuum Corp. Nd:YAG oscillator/amplifier laser with temperature stabilized second, third, and fourth harmonic generators capable of providing 170 mJ/pulse at 355 nm and 60 mJ/pulse at 266 nm. A Scientech UV power meter is used for laser tuneup. As shown, a 1 m focal length lens focuses the laser beam onto the target through a UV-grade quartz window at 45° incidence. The target was a CVD polycrystalline 3C-SiC mirror blank (Morton Advanced Materials) chosen for its high purity (99.9995%) and density (near theoretical). A single-axis mirror scanner rasters the laser beam across the target, resulting in a 6 mm long ablation pattern. The fluence is varied by adjusting the lens to target distance and the resulting plume is directed towards the substrate. The deposition chamber is a standard 6-way stainless steel cross (6 inch diameter) modified to include a small flange at 45° for laser beam access. A 700 l/s diffusion pump provides a base pressure of 10^{-7} Torr.

For Phase I, several modifications to the facility were made to improve our control of the process variables. The substrate/heater was mounted on a linear feedthrough to allow the target to substrate distance to be accurately set. The target was also mounted on a linear feedthrough to allow rapid target switching. In addition, this enabled us to avoid previous ablation burn patterns by slightly adjusting the target with respect to the laser beam. It was necessary, however, to periodically sand the SiC target to provide a "fresh" surface for PLD. Sanding the target was accomplished by manual grinding with a 270 grit diamond sharpener. Inevitably, fine dusts from the sanding process remain on the target surface. Removing the dusts with solvent is unacceptable because of possible residue contamination. Therefore, a pre-ablation shutter mounted on a rotary feedthrough was installed for pre-deposition cleaning (pre-ablation) of the target. For each experiment, the substrate was blocked by the shutter immediately before deposition during pre-ablation of the target (~ 100 pulses). These modifications are depicted in Figure 1.

A silicon carbide element heater was utilized to radiatively heat the Si and 6 H-SiC substrates to 1000° C. Higher substrate temperatures were obtained by installing a tungsten wire coil between the target and the substrate. This combined heating arrangement enabled substrate temperatures as high as 1220° C to be realized. Substrate temperatures for all depositions were determined by a calibrated Minolta-land pyrometer (1.1 μ m) which viewed the substrate through an Infrasil Quartz window at 55° to the substrate normal. The temperature determination of Si was verified by comparing the value obtained with the pyrometer (emissivity = .65) to that obtained with a thermocouple bonded to the Si front surface with conductive silver paint. The .65 emissivity value was chosen from the literature (27) and is known to be constant above 600° C. Good agreement between the pyrometer and the thermocouple was obtained.

For SiC substrate temperature measurements, it was necessary to measure the SiC emissivity at 1.1 μ m as a function of temperature in order to determine the correct emissivity value for the pyrometer. These measurements were made on a unique Bench-Top Emissometer, developed by AFR, which simultaneously measures temperature and emissivity of materials at elevated temperatures (28). At temperatures ranging

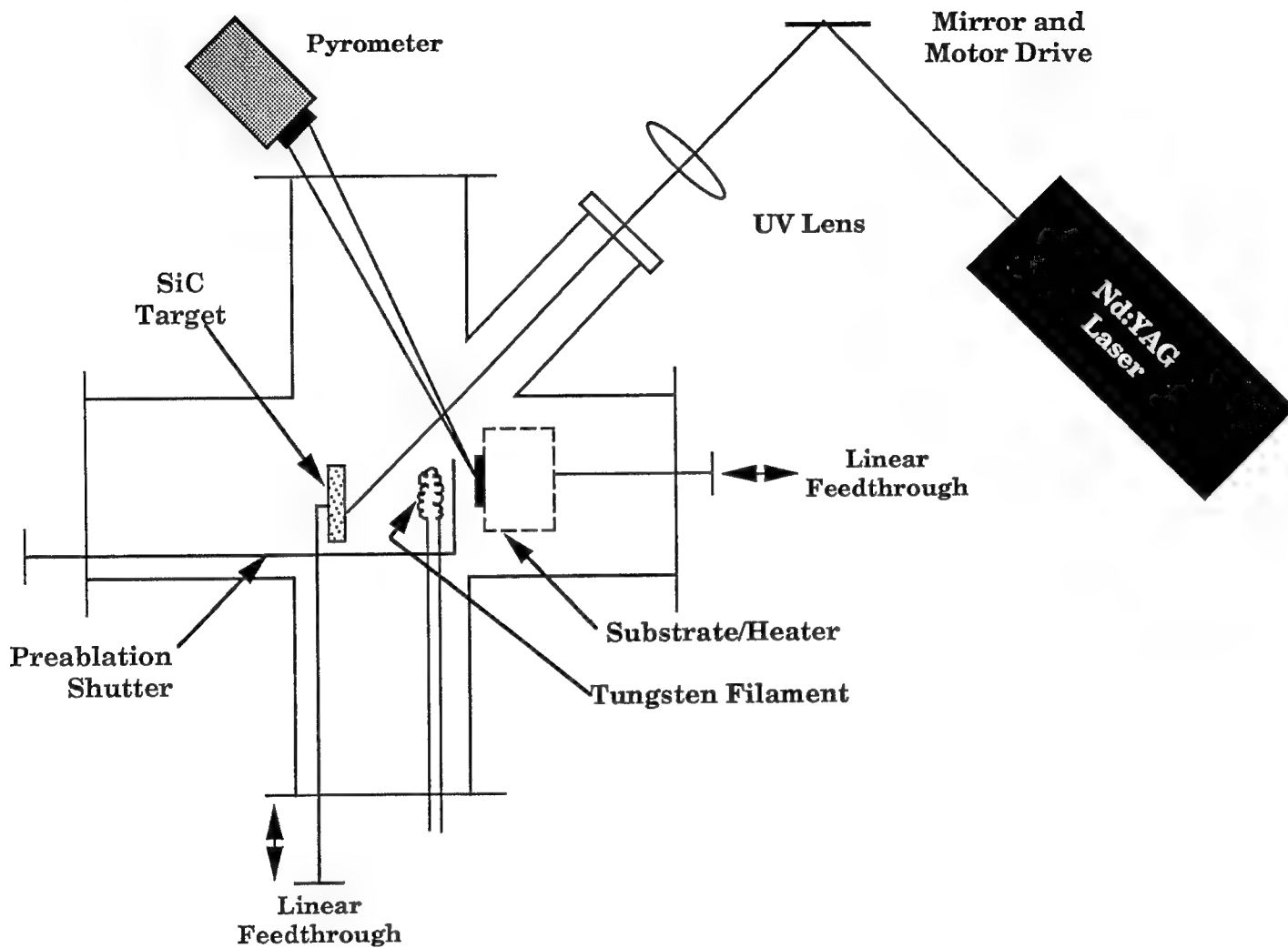


Figure 1. SiC Pulsed Laser Deposition System Employed in Phase I.

from 514° C to 1094° C, the emissivity of the SiC substrate at 1.1 μm was determined to be a constant of $\sim .23$. At these temperatures, the transmittance at 1.1 μm was measured to be $\sim 48\%$. This result indicated that pyrometry measurements of the SiC substrate in our deposition chamber would be erroneous because the pyrometer would partially “see” the silicon carbide heating element located behind the substrate. To correct this, the back sides of the SiC substrates were coated with a thin layer of graphite paint prior to deposition. Not only did the graphite coat make the SiC substrates optically opaque, it also improved the radiative transfer from the heater to the substrate because of its much higher emissivity of an estimated .95. A combined emissivity of .65 was chosen for the graphite-coated SiC substrates based on an analysis of their individual emissivities.

3.b. Task 2 - Prepare Substrates

Objective

Obtain 6H-SiC and Si substrates of various orientations and prepare for deposition by the spin etch method.

Results

The substrates used for SiC thin film deposition were 6H-SiC (0001) (Si face), vicinal 6H-SiC (0001) polished 3.5° towards [1120], Si (100) and “SIMOX” substrates. The 6H-SiC substrates were n-type, research grade provided by Cree Research, Inc. cut into 5x10 mm chips. Research grade is classified as having greater than 70% usable 6H surface area, along with striations and other SiC polytypes. The SIMOX substrates with an 80 nm thick oxide layer buried 180 nm into a Si (100) wafer were obtained from Soitec.

Substrate Preparation - To achieve good epitaxy between the SiC film and substrate, it is important to remove the native oxide layer from the Si or SiC substrate prior to growth. Researchers have observed that the method of substrate preparation prior to deposition may significantly affect the quality and polytype of SiC films grown on 6H-SiC substrates. Although the data were not conclusive, Powel et al. (5) observed that surface pretreatments such as polishing, oxidation, and HF etching appeared to increase the density of DPB's in 3C-SiC films grown on 6H-SiC substrates. Rowland et al. (18) has suggested that the resulting polytype (3C vs 6H) may also depend on the surface pretreatment.

The “spin etch technique” has proven to be an extremely effective method of removing the native oxide from Si substrates. The chemical similarities of the oxidized (111) Si surface and the oxidized (0001) Si face of the 6H-SiC permit etching and passivation of the 6H-SiC surface with HF (6). We therefore believe that the Si spin etch technique should be adaptable to 6H-SiC (0001) substrates.

In Phase I, all Si and 6H-SiC substrates were prepared by the spin-etch technique. The method used at AFR is very similar to that described by Fenner et al. (7) for preparing Si substrates. Prior to the spin-etch, the wafers are cleaned of particle contamination and degreased in a series of high purity organic solvent washings. We then spin etch the wafer using a 1:1:10 solution of HF (semiconductor grade), water (HPLC grade), and absolute reagent alcohol (HPLC grade). The high purities are necessary to avoid recontaminating the wafer. As shown in Figure 2, the etching takes place in a small hood purged with N_2 , and a pipette dispenses the etchant drop by drop, letting each drop evaporate from the wafer before adding the next. Dipping the wafer is unacceptable because the wafer picks up a Langmuir-Blodgett film of contaminants collected at the liquid surface. At this point, the spin etched wafer is hydrogen terminated

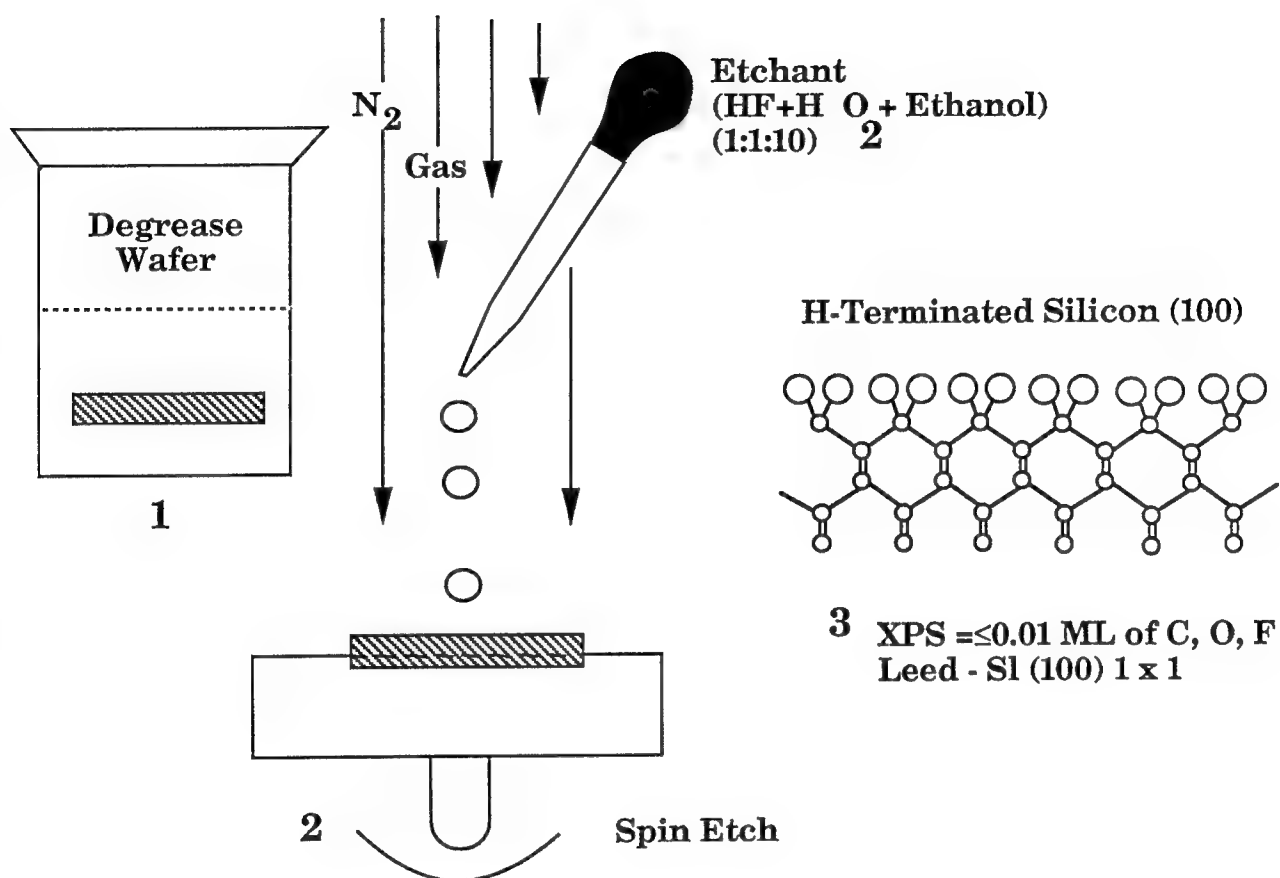


Figure 2. Diagram of the Spin Etch System.

and unreconstructed (i.e., 1×1). The hydrogen termination remains intact under vacuum at temperatures less than 550°C . XPS has determined that the total C, O, and F residue is on the order of 0.001 - 0.05 monolayer.

3.c. Task 3 - Deposit Thin Films of 3C-SiC on 6H-SiC and Si

Objective

Deposit high quality films of SiC on 6H-SiC and Si substrates by Pulsed Laser Deposition.

Results

Our approach was to explore various PLD process variables to determine the best operating conditions for depositing epitaxial SiC thin films on Si substrates. Results obtained for Task 4 (Analysis of 3C-SiC films guided the optimization process. We would then use those conditions as a starting point for subsequent depositions on the more costly 6H-SiC substrates. For all experiments, the following PLD parameters were held constant:

- Laser wavelength = 266 nm.
- Total laser pulse energy $\sim 47\text{ mJ}$
- Pulse Repetition Rate = 10 Hz
- Target to substrate distance = 5 cm

The deposition parameters that were investigated included, 1) Background pressure, i.e. deposition in vacuum or in the presence of a background gas in an effort to reduce the pitting observed in SiC films grown on Si (100), 2) laser fluence at the target and, 3) substrate temperature. The list below summarizes the results of SiC films produced as the deposition parameters were varied. Detailed analyses of the films are described in Task 4 Results (Section 2.d.).

- ⇒ Background Pressure - SiC films grown on Si (100) substrates in vacuum displayed a pitted morphology at temperatures greater than 900°C , an effect which has been observed by others (29). We believe that the pitting is caused by a reaction between the Si surface and carbon containing impurity (diffusion pump oil vapor) and oxygen impurity (water vapor) in our vacuum system. To confirm this, we heated a Si substrate to 930°C for 10 minutes at 10^{-7} to 10^{-6} Torr, with no PLD. SEM revealed the presence of pits in the Si surface. Furthermore, a thin layer of SiC was formed as determined by FT-IR spectroscopy. For comparison, we heated a Si substrate to 930°C in an oil-free turbomolecular pumped vacuum system and found no evidence of void or SiC formation. In order to minimize the pit formation, several depositions in H_2 were attempted at pressures from 10^{-5} Torr to 50 m Torr. Chiu et. al. (29) have demonstrated that void formation from the reaction of C_2H_2 and Si substrates at 950°C can be suppressed in the presence of H_2 . In our case, no significant effect on void formation was observed. We also attempted depositions in argon and again, no suppression of the pit formation was observed. No pitting was observed, however, in SiC films grown on 6H-SiC substrates, even at temperatures as high as 1220°C . Clearly, depositing in an ultraclean

environment is warranted, hence our proposal to upgrade our system to an ultra-high vacuum system for Phase II research.

- ⇒ Laser Fluence - The quality of SiC films grown on Si (100) at 930° C was explored over a range of 1.5 - 14 J/cm². The films were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared (FT-IR) Spectroscopy, Rutherford Backscattering Spectrometry (RBS) and Scanning Auger Microprobe (SAM). All crystalline films grown on Si (100) were determined to be the 3C (cubic) polytype. Films grown at 7 and 14 J/cm² were determined to be polycrystalline and/or amorphous. Films grown at 1.5, 2 and 2.8 J/cm² were well-oriented with respect to the Si substrate while the "best" films were grown at 1.5-2 J/cm².
- ⇒ Substrate Temperature - SiC film quality was also investigated as a function of growth temperature. SiC films grown from 855° C to 1055° C at 1.5 J/cm² showed improved crystalline quality with increasing substrate temperature, as determined by XRD and FT-IR measurements. XRD Phi scans established the epitaxial relationship of the SiC films with the Si (100) substrates. Higher growth temperatures were required for single crystal growth of SiC films on 6H-SiC substrates. Films grown on 6H-SiC (0001) substrates at temperatures of 1050-1100° C were measured by XRD and interpreted as 3C-SiC, with a preferred <111> texture. More work is required to determine the degree of in-plane orientation for these films. Films grown at ~ 1200° on 6H-SiC (0001) and vicinal 6H-SiC (0001) oriented 3.5° towards [1120] were analyzed by cross-section Transmission Electron Microscopy (XTEM) and Selected Area Electron Diffraction and determined to be single crystal 3C-SiC.

3.d. Task 4 - Analysis of SiC Films

Objective

Apply a variety of structural, compositional, and electrical analyses to determine the quality of the deposited films. Perform analyses continuously as feedback to guide experimental parameters.

Results

SEM Results - Scanning Electron Microscopy (SEM) revealed a pitted morphology of the SiC film and Si (100) substrates for depositions above 900° C. As shown in Figure 3, the surface of the substrate is dimpled with pyramidal-shaped pits in the film and substrate. The sides of the pits are parallel to other pits and parallel to the cleavage planes of the Si (100) wafer. In an effort to minimize the out-diffusion of Si from the Si substrate during deposition, we also deposited on the SIMOX wafers, which contain a buried oxide layer 180 nm below the surface. No reduction in pit formation was observed. In contrast to films grown on Si substrates, SiC films on SiC substrates showed no evidence of pitting of either the film or substrate at temperatures up to 1200° C. Figure 4 presents SEM photographs of SiC films grown on 6H-SiC and vicinal 6H-SiC substrates at 1175° C and 1200° C respectively. Although the films contain no pits, their morphology is rough, more so for the film grown on the on-axis 6H-SiC (Figure 4a). Films grown on 6H-SiC substrates at temperatures below 1100° C were much smoother, which has also been observed by Rowland et al. (18).

A particularly promising result revealed by the SEM images in Figures 3 and 4 is that the films are essentially particle free. These images are quite representative of the entire film. As mentioned earlier, a problem that often occurs in PLD is the co-deposition of particles with the film, which can seriously

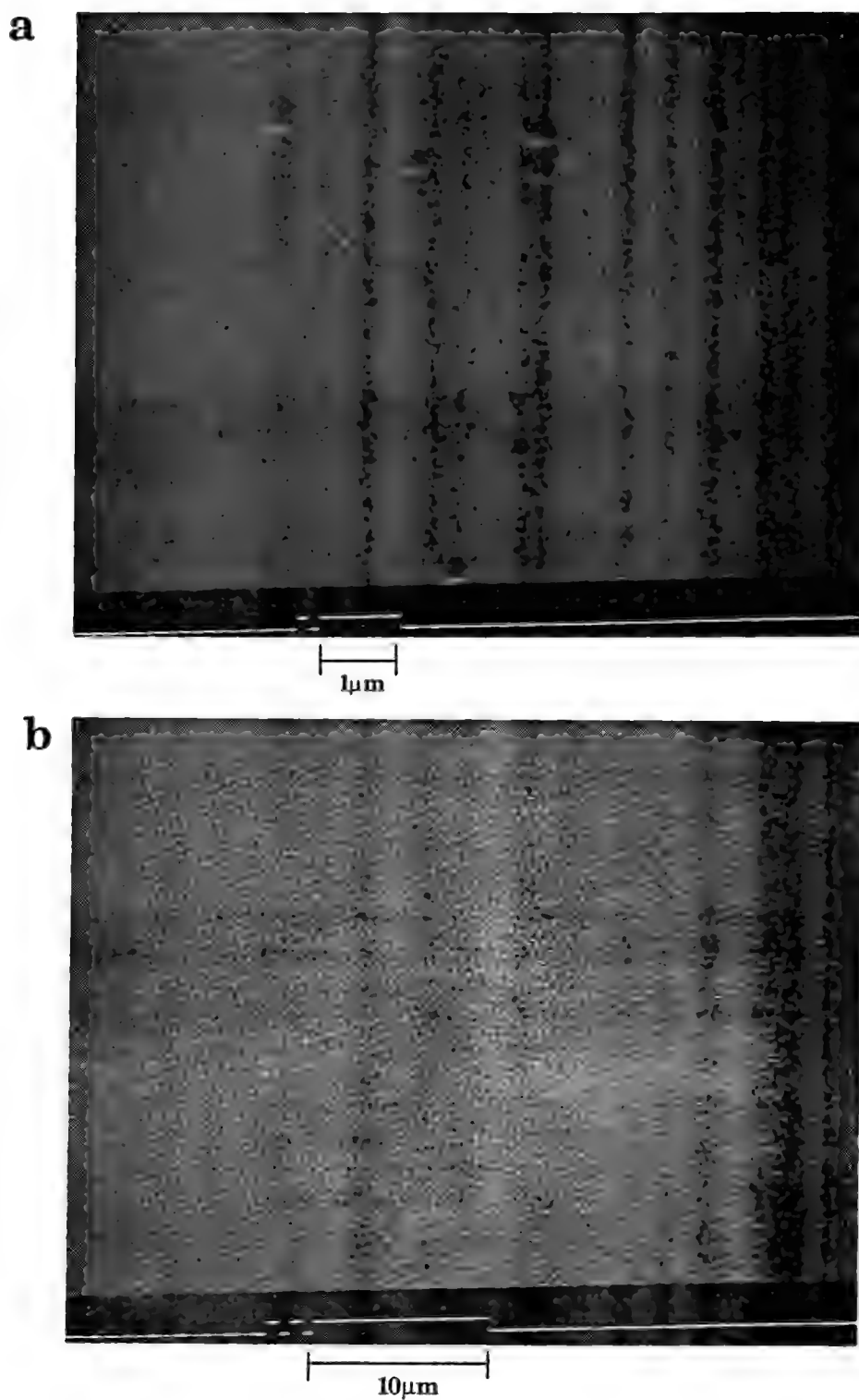


Figure 3. SEM Images of a SiC Film Grown on Si(100) at 1.5 J/cm^2 .
a) 14,000 X; b) 2800 X. Note the Absence of Particulate Growth.

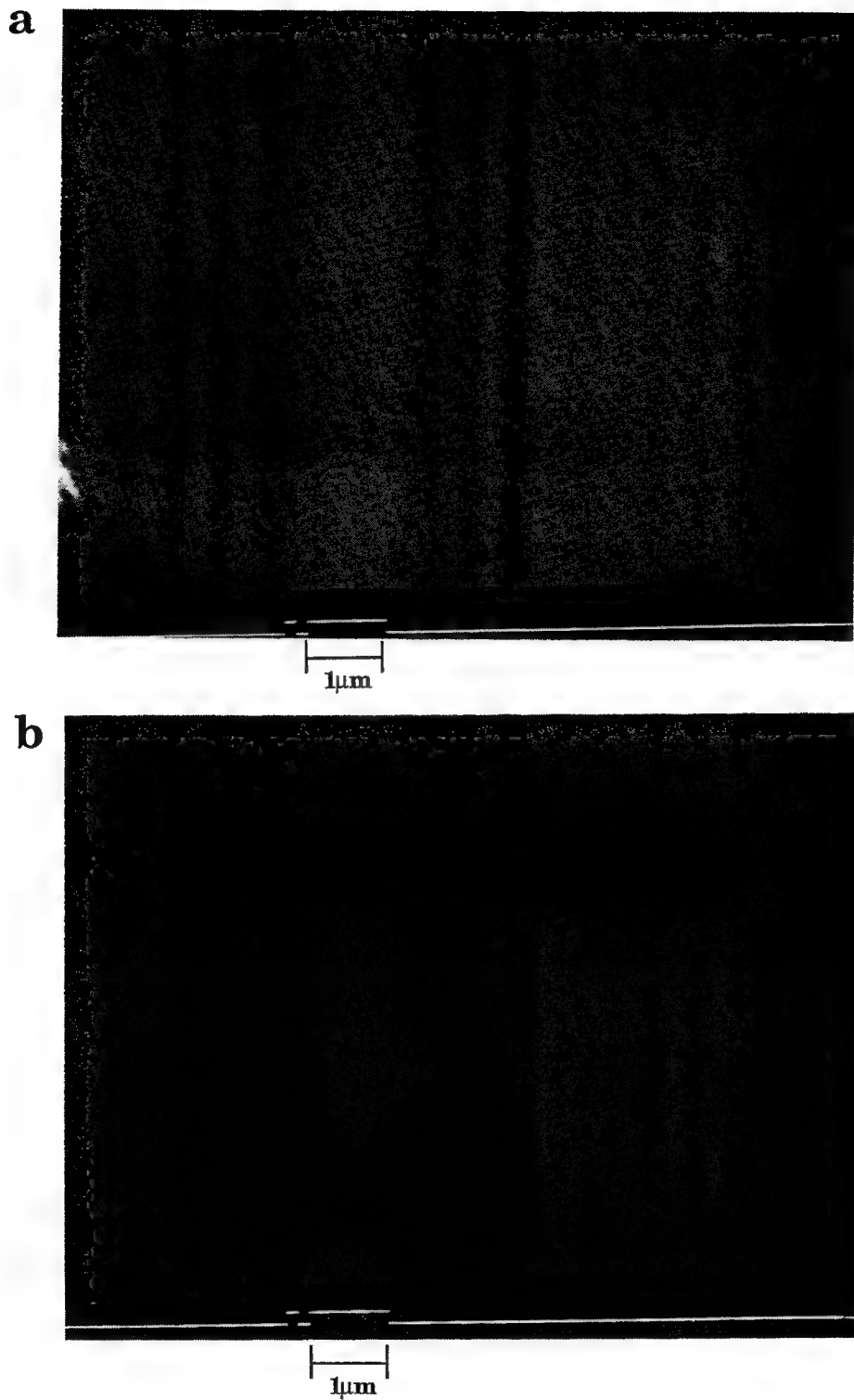


Figure 4. SEM Images of a 3C-SiC Thin Films Grown by PLD at 1200°C on a) 6H-SiC(0001) Substrate and b) Vicinal 6H-SiC(0001) Oriented 3.5° Towards $[11\bar{2}0]$.

degrade the electronic properties of thin film devices. Choosing suitable deposition conditions, however, can avoid particle depositions. The absence of particles in these films can be attributed to the short laser wavelength (266 nm), the moderate laser fluences (1.5-2 J/cm²) and the use of a high density target (near theoretical).

RBS and SAM Results - Film composition was measured to ascertain the effects of laser fluence on film quality. We suspected that the poor film quality at high laser fluences was caused by gross departures in stoichiometry. Rutherford Backscattering Spectrometry (RBS) measurements were obtained for the films grown at 2 J/cm² and 7 J/cm² and are shown in Figure 5. The C/Si ratios were determined to be 1.132 and 1.325 for the films grown at 2 and 7 J/cm², respectively. This result confirmed our suspicions, however, it also indicated that our "best" films were still significantly C rich. The source of extra carbon is most likely the oil vapor background present in our deposition chamber. Typical PLD operating conditions were at 10⁻⁷- 10⁻⁶ Torr. At these pressures the exposure of surfaces to contaminants in the chamber is roughly 1 monolayer/sec, which is on the order of our deposition rate. The likely presence of O₂ and H₂O in the chamber may react with the Si species in the plume to form SiO_x. At deposition temperatures above 900° C, SiO_x species are easily desorbed, which effectively makes the film Si lean. From these results it is clear that eliminating background impurities is critical to the success of Phase II, which further supports our proposal to improve the vacuum.

Modeling using the RUMP program, the RBS measurements yielded film thickness fits of 1574 Å and 1346 Å for the films grown at 2 and 7 J/cm², respectively. RBS can be very accurate, and here it is estimated to be within ± 2 Å. From this data, our deposition rates were determined to be 1 - 1.5 Å/sec at a repetition rate of 10 Hz, which is consistent with the deposition rates of other films, such as YBaCuO, grown at AFR.

In order to investigate the relative changes in composition as a function of depth in the films, a Scanning Auger Microprobe (SAM) analysis was performed on a SiC film grown on Si (100) at 1.5 J/cm² and on the CVD SiC target. Figure 6 presents the Si/C percent concentrations as a function of depth. For this analysis, the probe size was 10 µm and Auger spectra were obtained at 100 Å intervals. Essentially no change in composition is detected in the top 400 Å of the film. At 600 Å, we are probably measuring the Si substrate. These results indicate that the deposition was quite uniform. Also, no oxygen is present, (within instrumental noise) especially at the interface region. It is interesting that the top 200 Å of the target is severely C rich, although the Si/C ratio becomes stoichiometric at 500 Å and deeper. It is possible that very fine particles of diamond remain after the target surface is sanded to remove ablation patterns. In any case, pre-ablating the target prior to deposition is justified. We also observe that the concentration of O is surprisingly high in the target.

One should note that although the SAM analysis indicates that the Si/C ratio is Si-rich, these results should be interpreted with caution. SAM is useful in making relative concentration measurements, however, the RBS measurements have better absolute accuracy.

XRD Results - XRD patterns for several SiC films on Si (100) grown at different laser fluences were obtained from Materials Analysis Group (MAG) in California. No SiC reflections were observed by θ -2 θ scans of films grown at 7 and 14 J/cm² at temperatures of 800°-1030° C. Glancing incidence XRD patterns for these films grown above 930° C, shown in Figure 7, reveal a peak at 2 θ =35.4° which corresponds to the (111) reflection of 3C-SiC. For each pattern, vertical lines are shown that mark the possible reflections and their relative intensities for 3C-SiC. The films grown at 7 J/cm² are more crystalline than those grown at 14 J/cm², as evidenced by their much stronger SiC (111) peak. Because no peaks are observed in the

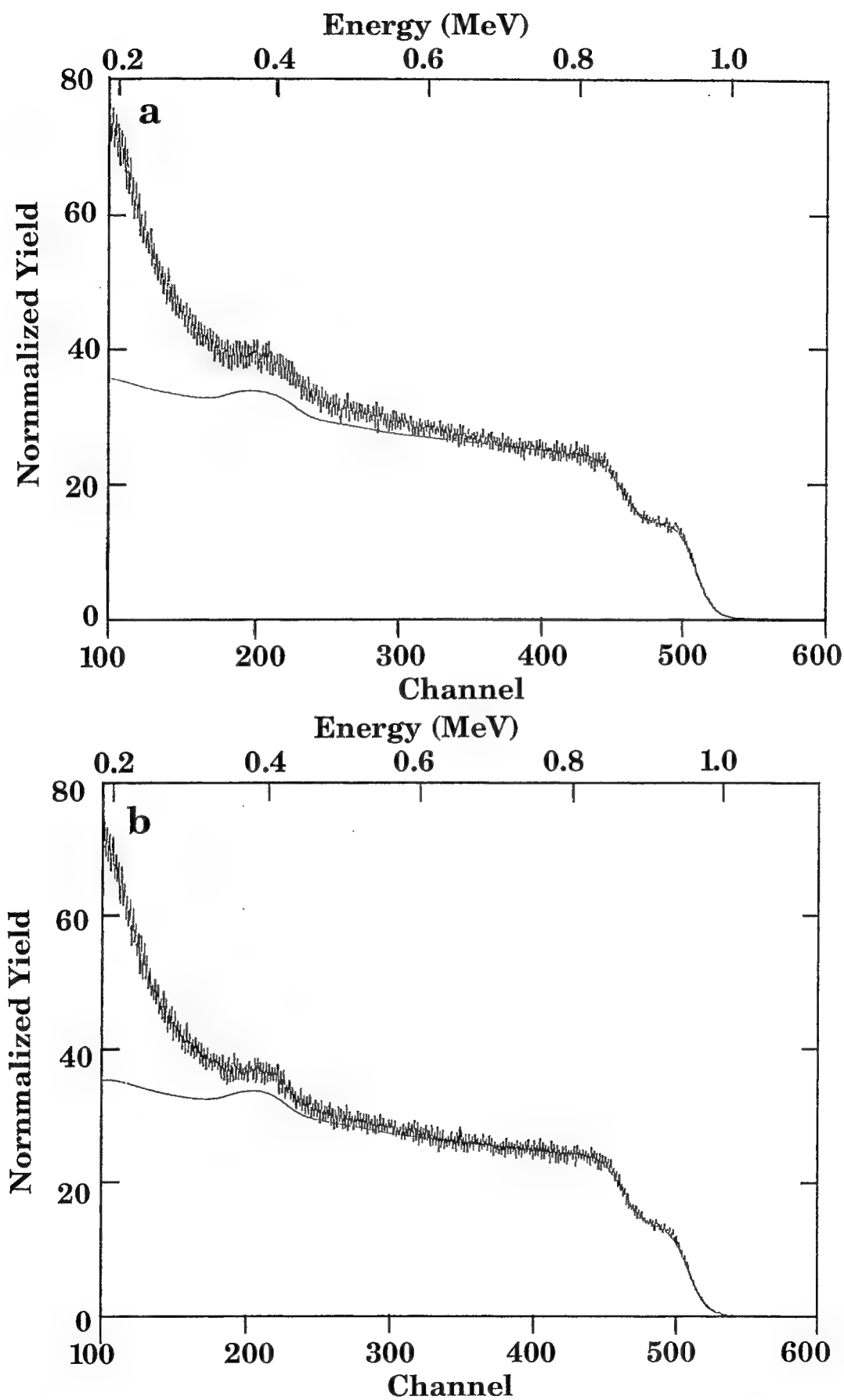


Figure 5. Rutherford Backscattering Spectra for SiC Films Grown on Si(100) at a) Laser Fluence of $2\text{J}/\text{cm}^2$ and b) Laser Fluence of $7\text{J}/\text{cm}^2$. The Smooth Curve is the RUMP Fit for Film Thickness.

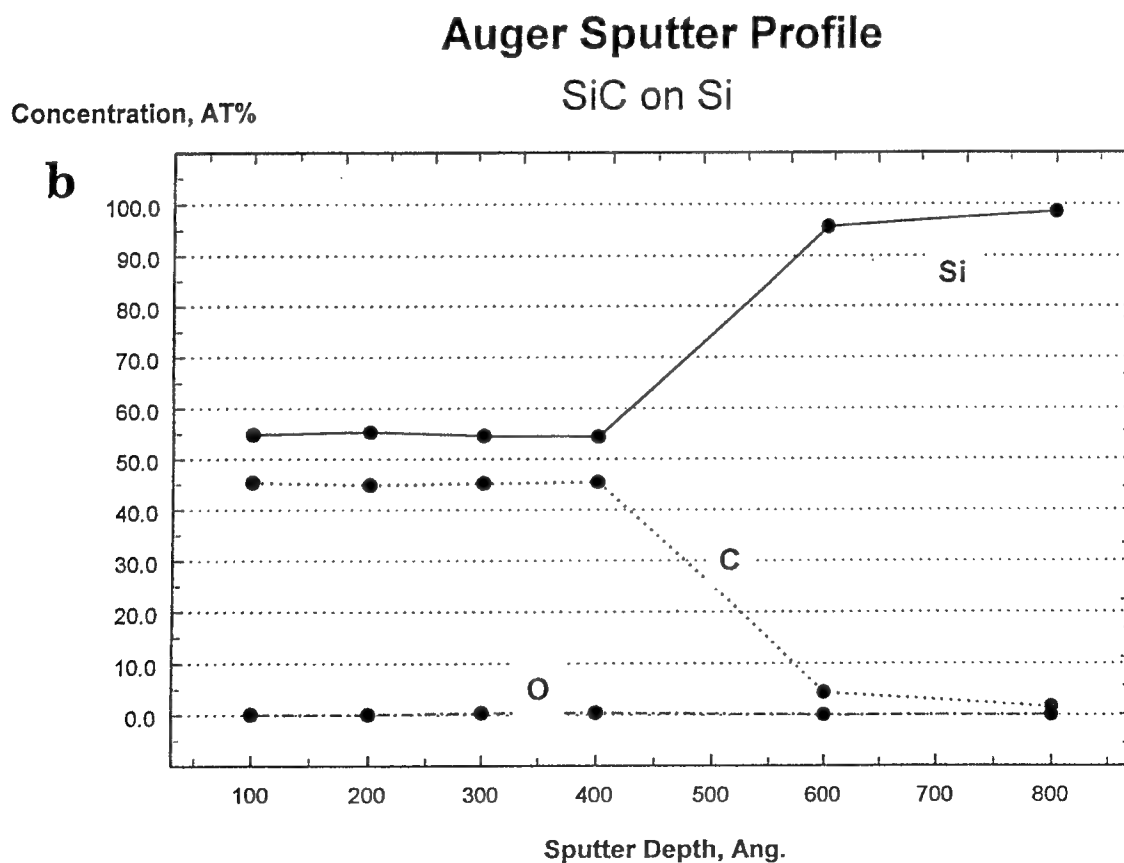
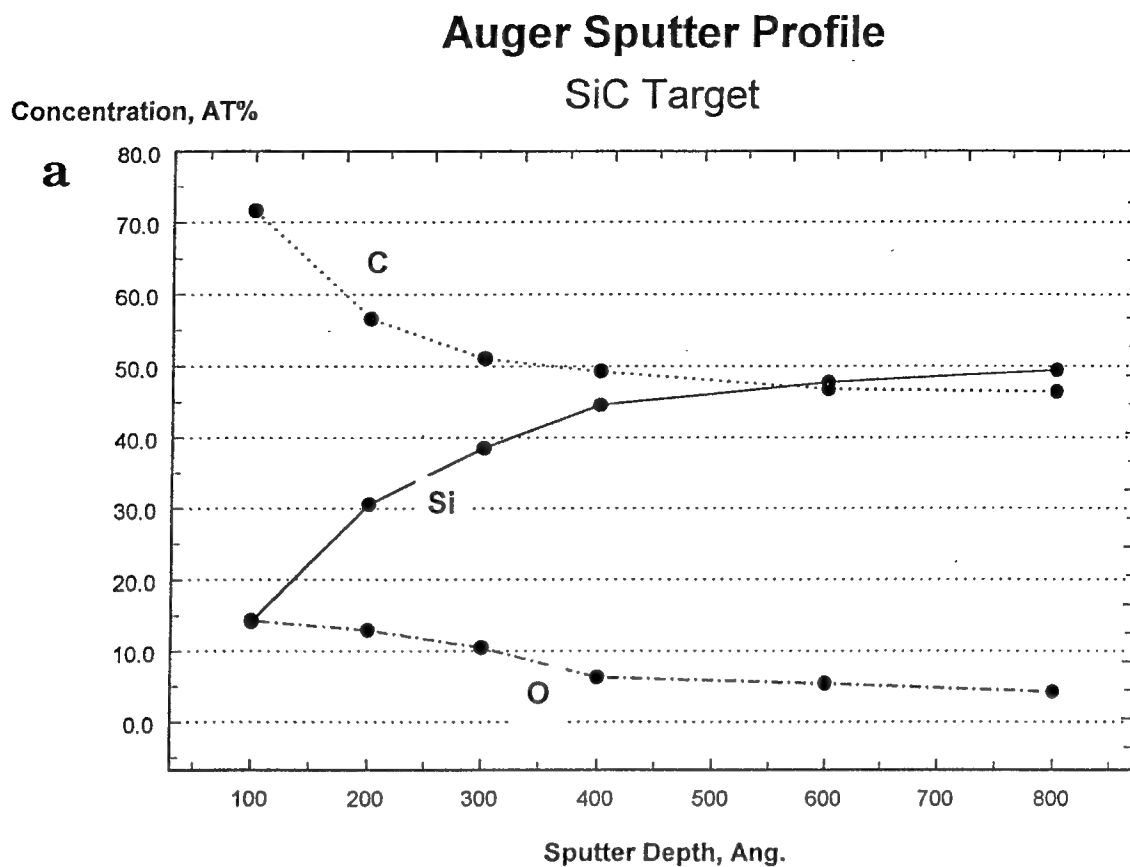


Figure 6. Scanning Auger Microprobe Sputter Profile as a Function of Depth for a) CVD SiC Target and b) 3C-SiC Film Grown at 930°C at 1.5J/cm².

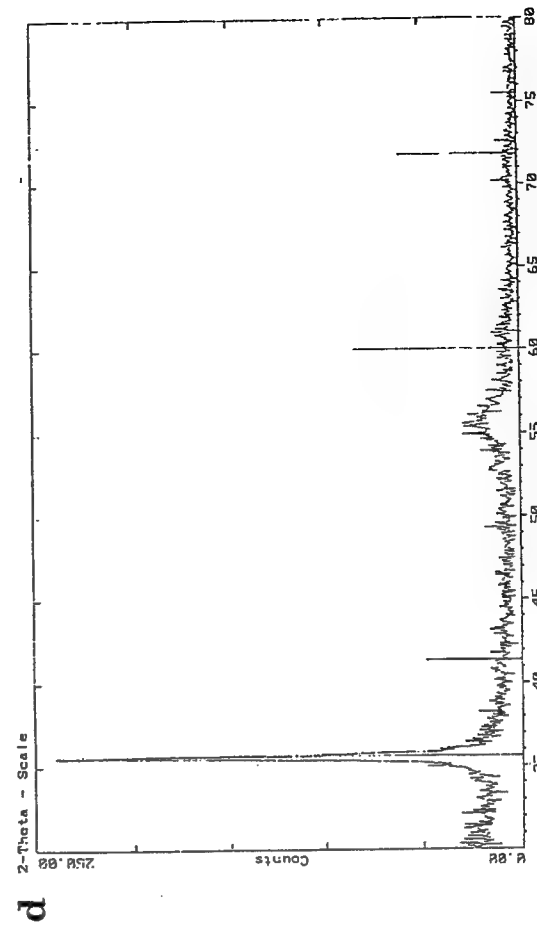
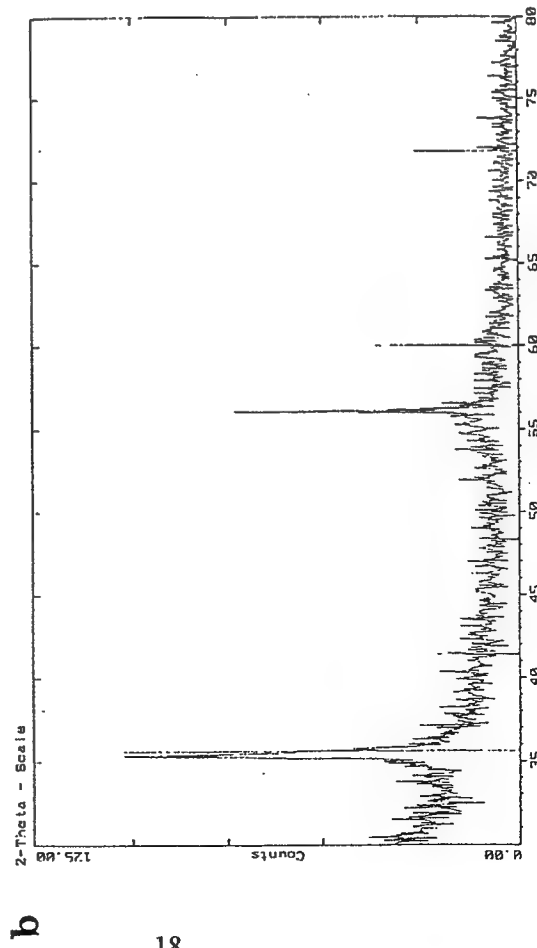
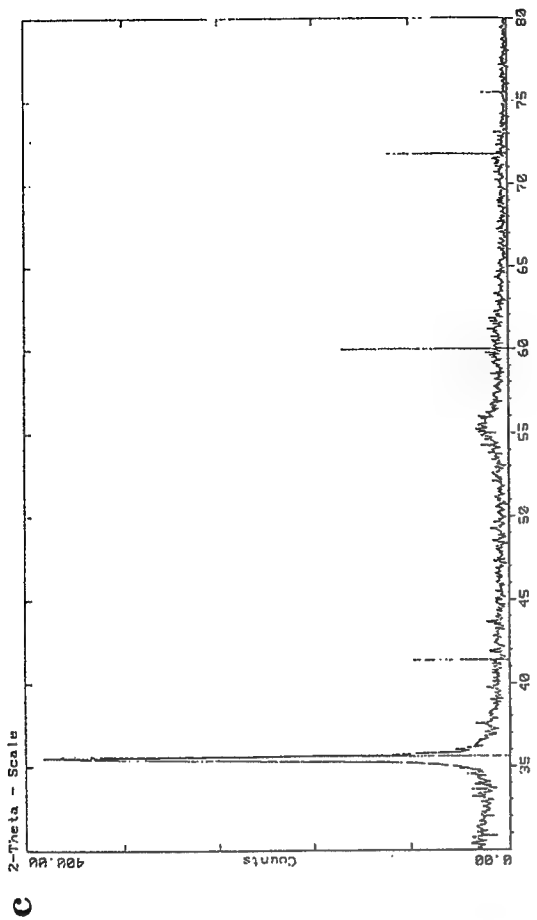
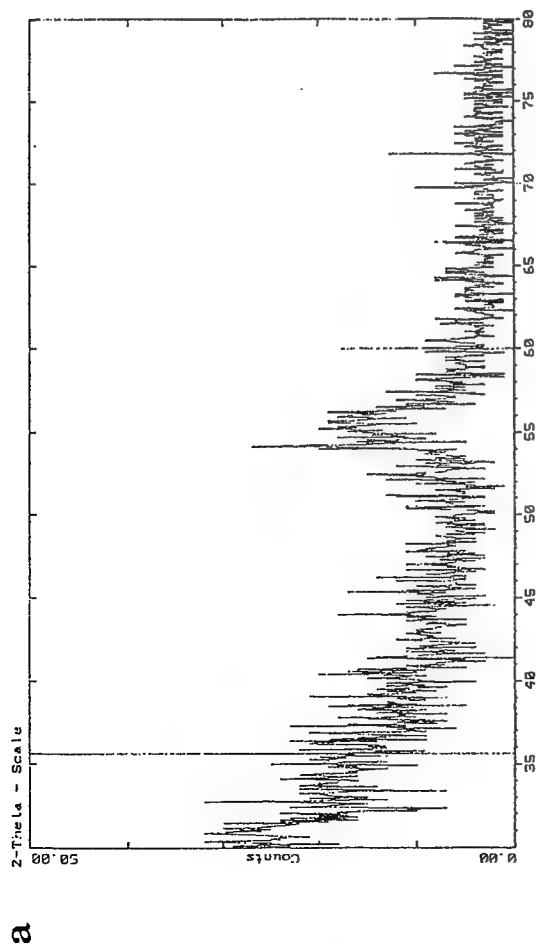


Figure 7. Glancing X-Ray Diffraction Patterns for SiC Films Grown at a) 800 °C With an Energy Density of 14 J/cm² at the Target, b) 930 °C With an Energy Density of 14 J/cm² at the Target, c) 930 °C With an Energy Density of 7 J/cm², and d) 1030 °C With an Energy Density of 7 J/cm². All Films Were Grown on Si(100).

θ -2 θ scans, however, all of the films can be characterized as lacking orientation with respect to the Si (100). Figure 8 presents θ -2 θ scans for SiC films grown on Si (100) at laser fluences of 2.8, 2.0 and 1.5 J/cm². The growth temperature was 930° C. Each pattern shows a 3C-SiC (200) peak at 2 θ =41.5°. No peak at 2 θ =35.4° is observed, which would correspond to a 3C-SiC (111) reflection. Two minor features at 33° and 61.8° are the Si (200) and β -Si (400) reflections, respectively. The Si (200) reflection is normally forbidden because of crystalline symmetry. Strain at the SiC/Si interface, however, may break the symmetry near the surface and allow a low intensity Si (200) reflection to occur. These results indicate that the films are well oriented with respect to the substrate. XRD rocking curves, shown in Figure 9, were then obtained in order to gauge the defects and strain associated with each film. The full width at half maximum (FWHM) was measured to be 1.45° for the films grown at 2 and 1.5 J/cm² and 1.63° for the film grown at 2.8 J/cm². This data indicates that the "best" SiC films were grown at 1.5-2 J/cm², which was also supported by qualitative comparisons of the film's FT-IR reflectance measurements (discussed below).

SiC film quality was also investigated as a function of growth temperature. Three SiC films on Si (100) grown at 855° C, 930° C, and 1055° C at 1.5 J/cm² were analyzed by XRD by Dr. Mike Capano at Wright Patterson Air Force Base. Some oriented 3C-SiC was measured on the film grown at 855° C, however, it was probably a minority phase. The best film was grown at 1055° C. This result was based on the FWHM of its (113) peak, which was ~ 1.1°. The FWHM of the film grown at 930° C was ~ 1.3°. XRD Phi scans were also obtained for these films in an effort to establish in-plane epitaxy. Figure 10a shows that the 3C-SiC (113) reflection for the film grown at 930° C occurs only at 90° intervals, which is expected for a cubic film (four-fold symmetry) grown epitaxially on a cubic substrate (Si (100)). Figure 10b includes the θ -2 θ scan for this film, which reveals only the 3C-SiC (200) peak at 2 θ =41.4° and the 3C-SiC (400) peak at 2 θ =90.0°. These data are conclusive evidence that the SiC film has grown epitaxially on the Si (100) substrate.

XRD data were obtained of SiC films grown on 6H-SiC (0001) substrates. A film grown at 1090° C was analyzed by Dr. Capano at Wright-Patterson AFB. Interpretation of the results was somewhat difficult because the film was almost indistinguishable from the substrate. Another film grown at 1060° C was analyzed by Materials Analysis Group. Figure 11 presents a θ -2 θ scan of the film grown at 1060° C. For comparison, a scan of the backside of the substrate is included and is slightly offset for clarity. The two peaks at 2 θ =35.65° and 2 θ =75.5° are observed to increase in amplitude and in peak width on the film side, indicating that a crystalline film has formed on the substrate. The peak observed on the backside of the 6H-SiC substrate at 2 θ =35.65 is puzzling in that it is not expected for a perfect single crystal 6H-SiC (0001) substrate. The closest 6H-SiC reflection is the (102) at 2 θ =35.729°, which would occur only in a polycrystalline sample. 3C-SiC (111) exhibits a reflection at 2 θ =35.598°. This data suggests that either some 3C-SiC and/or polycrystalline 6H-SiC is present in the substrate, which is consistent with typical specs of the research grade 6H-SiC (70% usable single crystal 6H). Unfortunately, interpretation of the XRD pattern for the film side is also ambiguous. The amplified and broadened peak at 2 θ =35.65 is unresolvable. Likewise, the expected reflections of 6H-SiC (0012) at 2 θ =75.656° and of 3C-SiC (222) at 2 θ =74.494° are indistinguishable in this data. Therefore, the SiC polytype of the film can not be conclusively assigned on the basis of only the XRD data. Based on the relatively low growth temperatures, however, and our TEM results of films grown at higher temperatures (discussed below), we would expect the film to be the 3C-SiC polytype. The data reveal no 3C-SiC (200) peak at 2 θ =41.5°, thus the film is not randomly oriented. Therefore, we tentatively assign this film as 3C-SiC with a preferred <111> texture

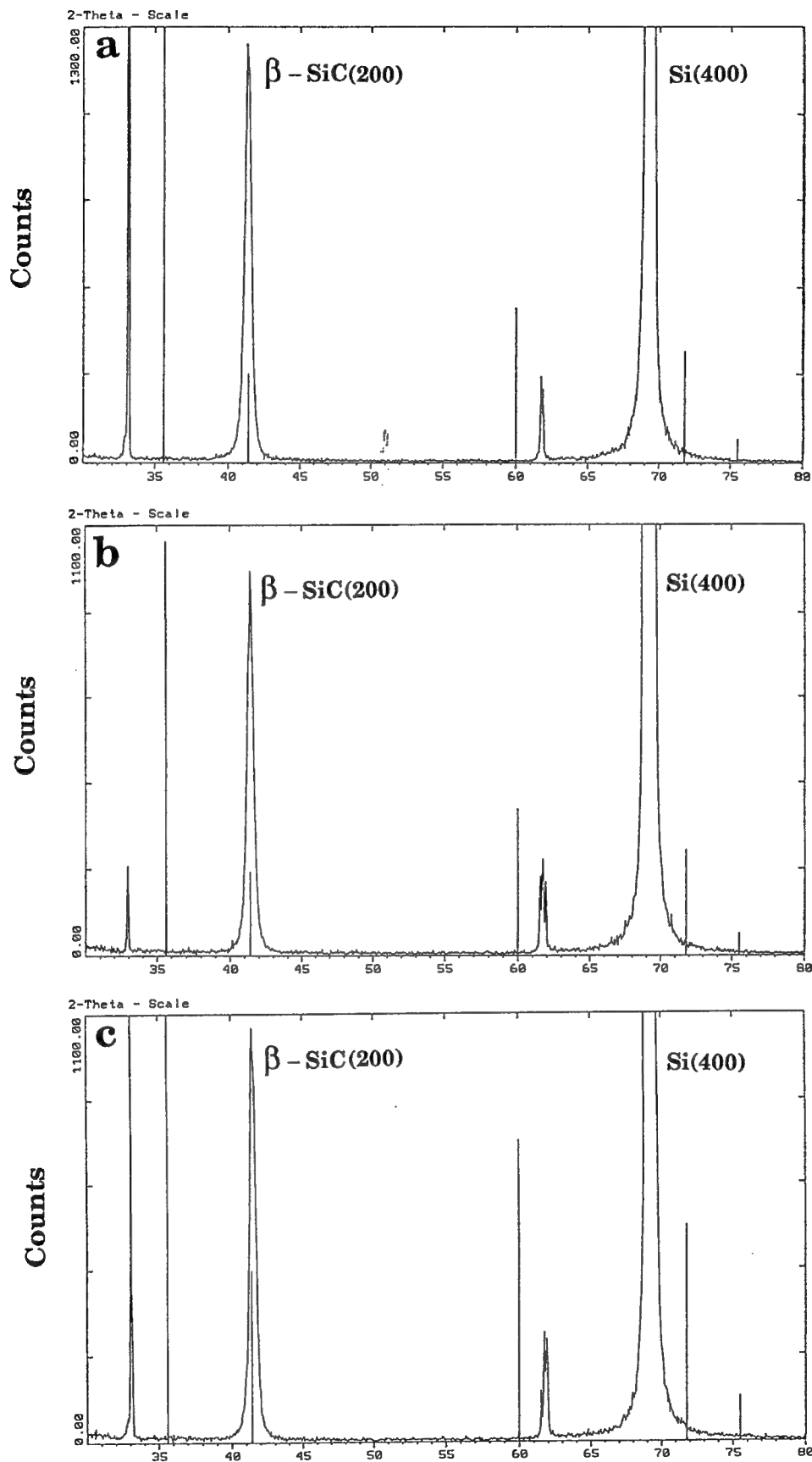


Figure 8. θ -2 θ X-Ray Diffraction Patterns of SiC Films Grown on Si(100) at 930°C with a Laser Fluence of a) 2.8 J/cm², b) 2.1 J/cm², c) 1.5 J/cm².

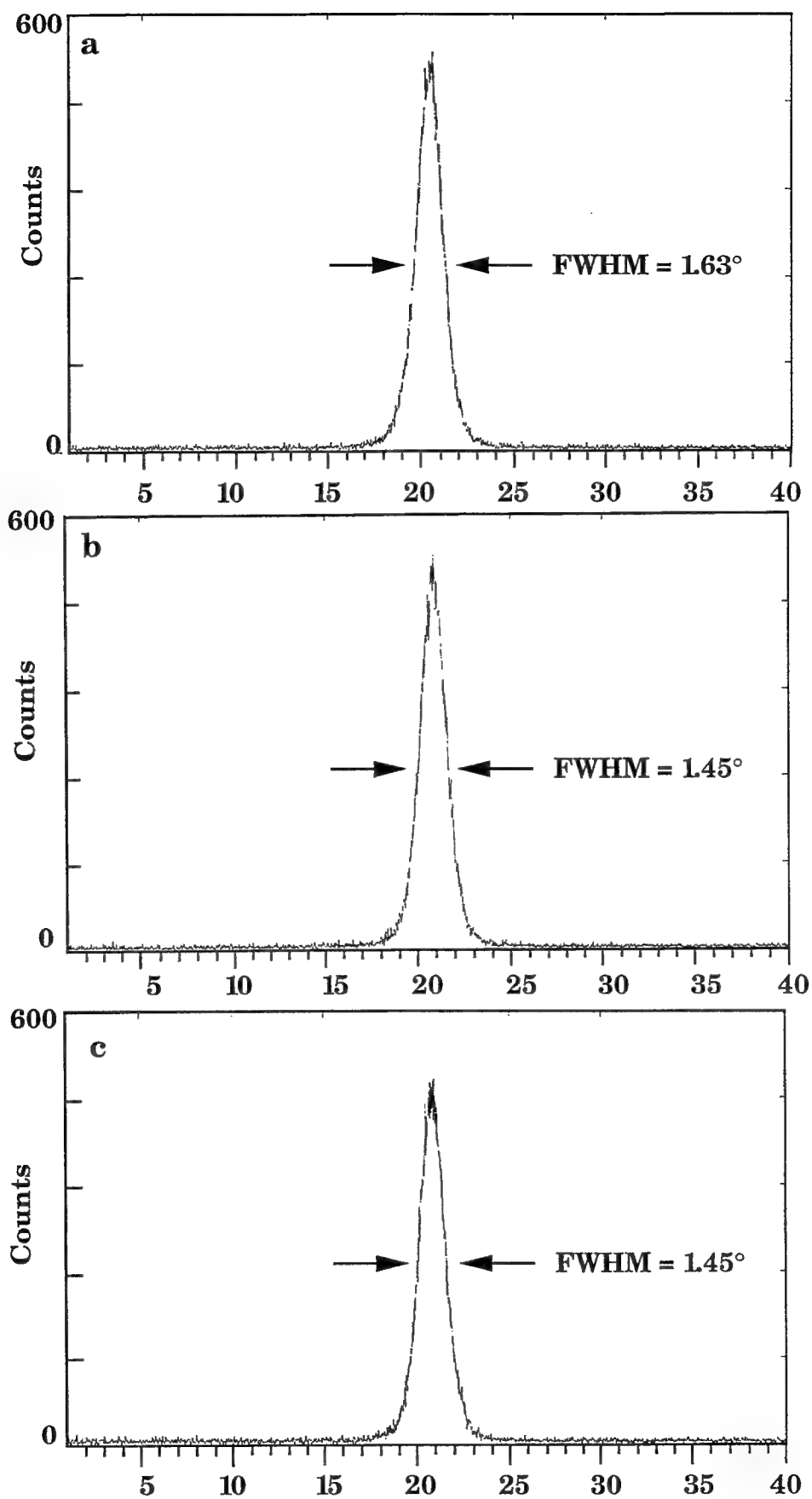


Figure 9. X-Ray Diffraction Rocking Curves of SiC Films Grown on Si (100) at 930°C with Laser Fluence of a) 2.8J/cm², b) 2.0 J/cm², and c) 1.5 J/cm².

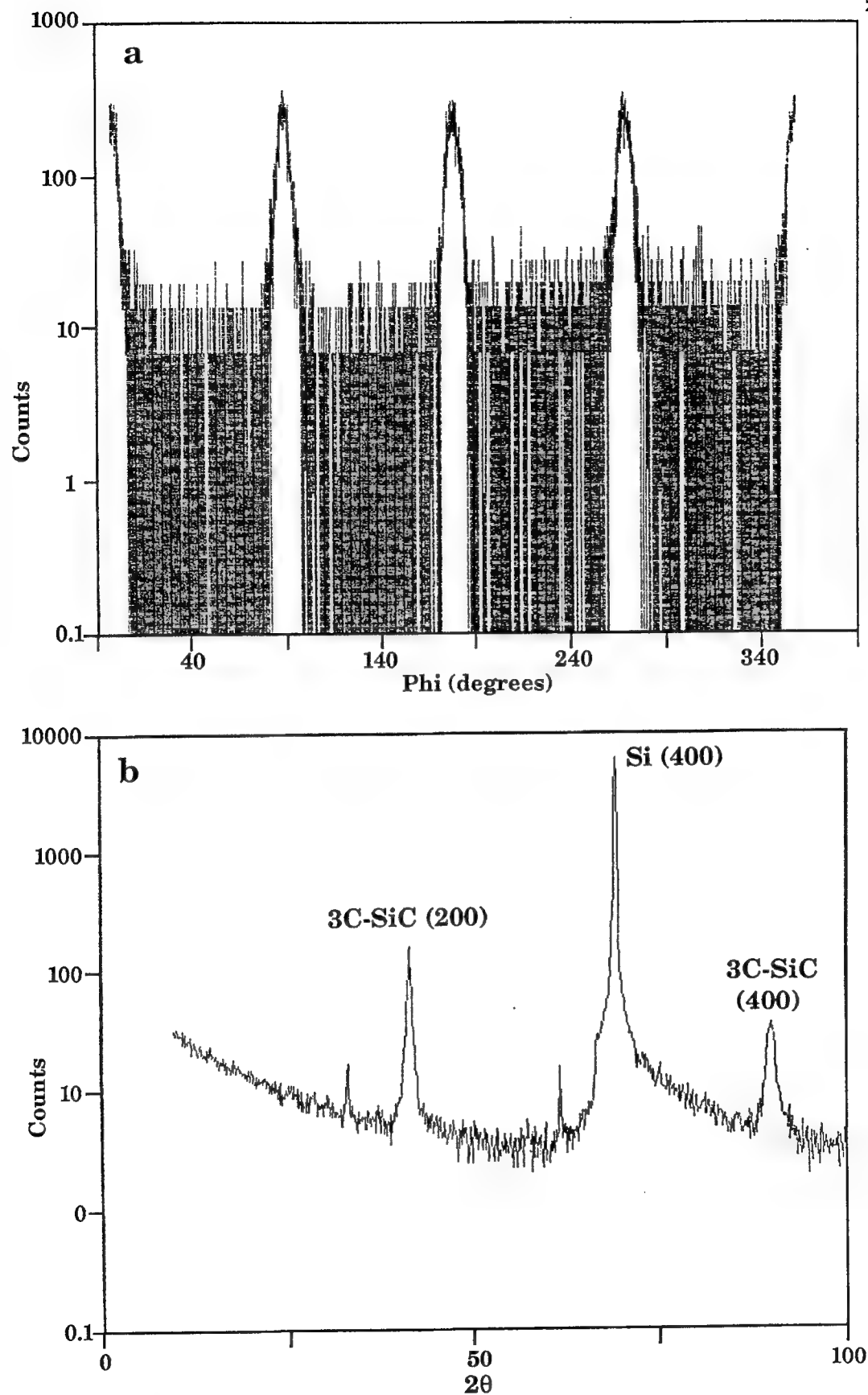


Figure 10. a) XRD Phi Scan of a SiC Film Grown at 930°C at $1.5\text{J}/\text{cm}^2$ on Si(100); b) θ - 2θ XRD Pattern of the Same Film.

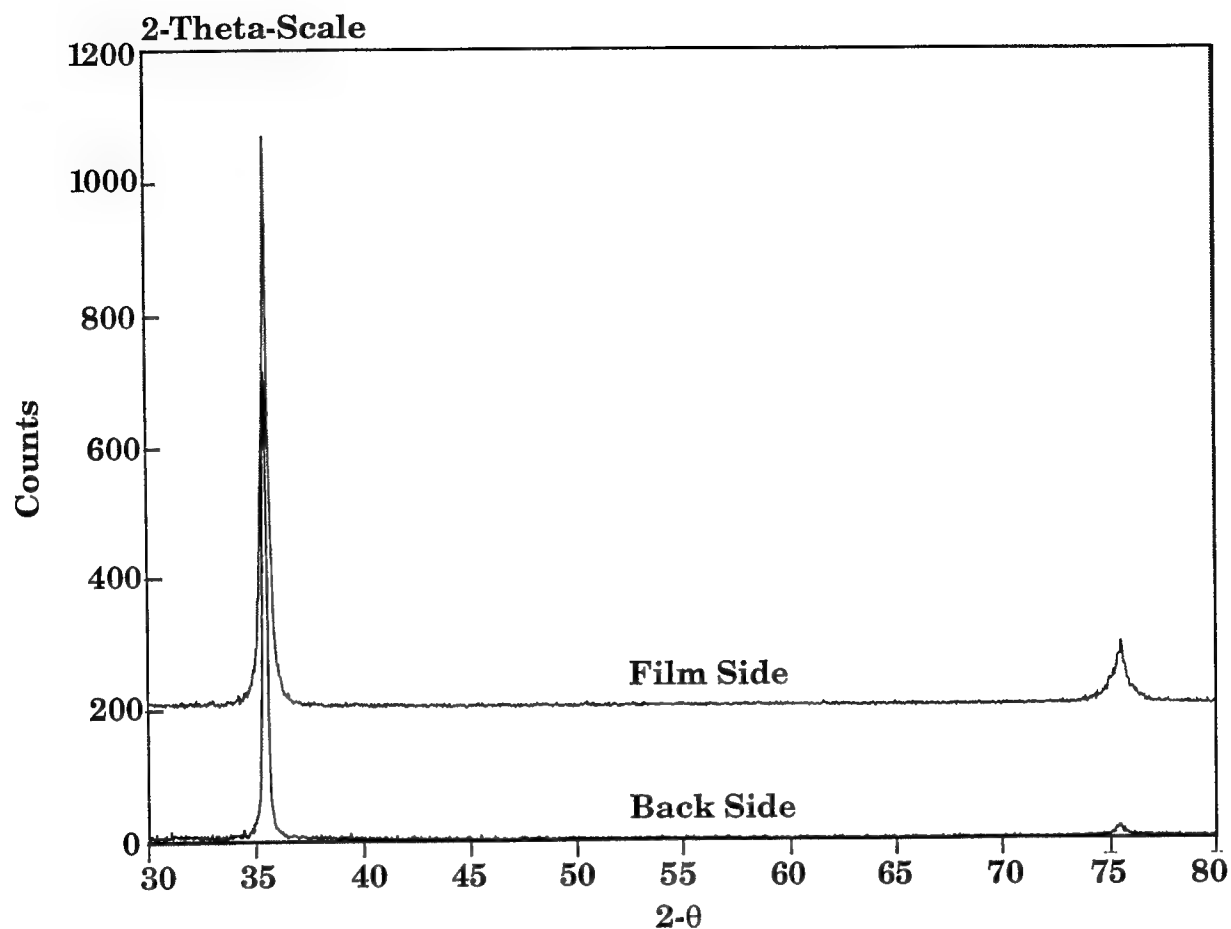


Figure 11. Comparison of XRD θ - 2θ Patterns Measured on the Film Side of a SiC Film Grown on a 6H-SiC (0001) Substrate at 1060°C and the Back Side of the Substrate. The Patterns are Offset for Clarity.

TEM Results - In an effort to improve crystallinity, a SiC film was deposited on the Si face of a 6H-SiC (0001) substrate at 1175° C. High resolution XTEM and SAED analyses were performed by STEM, Inc. in Woodbridge, CT. For sample preparation the specimen was cut in half and the surfaces with the films were glued with a conducting epoxy that was cured at 80° C for 2 hours. The glued sandwich was ground to a thickness of 1 mm and cut into strips, each 0.5 - 0.75 cm long and 2.5 mm wide. Each strip was embedded in a special 3 mm diameter hollow cylindrical holder using the same epoxy. 150-170 μ m thick discs were cut from the cylinder, one side was polished down to 0.05 μ m with aluminum oxide and the unpolished side was dimpled until perforation. The dimpled sample was milled using argon ions for 6 - 8 hours to obtain thin areas for TEM examination. In this geometry, the electron beam is parallel to the interface.

The film was characterized as single crystal 3C-SiC (111) accompanied by stacking faults and twins. Figure 12 displays the electron diffraction patterns obtained for the 6H-SiC substrate, the 3C-SiC film, and the film/substrate interface. A schematic illustration of the indexed pattern is shown with each electron diffraction pattern. Note that the pattern obtained at the interface is indexed as a perfect superposition of the [110] orientation of the film on the $[11\bar{2}0]$ substrate orientation. The reflections along the [0001]/[111] directions show no displacement, indicating a perfect match of the two lattices. For further illustration, Figure 13 presents the [0001] and [111] stereographic projections for the hexagonal and cubic lattices. Superposition of the projections demonstrates the perfect match along the $\langle 11\bar{2}0 \rangle$ and $\langle 110 \rangle$ directions. From these results, we conclude that $[110] \parallel [11\bar{2}0]$ and $(111) \parallel (0001)$ in the sample.

Many diffraction patterns of both the film and the interface were obtained from different regions of the sample and all yielded the same pattern, indicating that the entire film had the same orientation.

Figures 14 and 15 present high resolution XTEM images of the film and substrate. The TEM used in this analysis was not capable of producing atomic resolution images, however, close examination of the film (at the arrow) in Figure 14 reveals lattice fringes across the interface illustrating perfect continuity. The image in Figure 15 reveals defects, such as twins and stacking faults.

To enhance the resolution of the film/substrate interface and the film defects, atomic resolution TEM analysis of the film described above was performed by Professor Frederic Cosandey at Rutgers University in New Jersey. Figure 16 demonstrates perfect epitaxy of the 3C-SiC film on the 6H-SiC substrate. The interface, which is marked by arrows, is atomically abrupt. The lattice image of the substrate is somewhat diffuse, however, the 6H stacking sequence is clearly observed. Note that although the 3C-SiC film appears amorphous beyond the first ~ 50 Å of film, this is an artifact due to sample preparation (ion milling damage).

Figures 17 and 18 identify some of the defects which were typical of the sample. The lattice image of the SiC film in Figure 17 contains domains marked A and B which are rotated 180° along the (111) plane normal (double positioning). At the junction, there are stacking faults (SF) and twins (T) along the {111} planes of the two domains. Nearly all of the faults follow the {111} planes at an angle of 70.5° with respect to the substrate. In Figure 18, it is observed that the film contains faults in the 3 C stacking sequence which result in stacking fault boundaries (SFB) along the {111} plane. A twin parallel to the substrate that terminates within the film is also shown.

A SiC film deposited on a vicinal 6H-SiC (0001) substrate oriented 3.5° towards $[11\bar{2}0]$ at 1200° C was also analyzed by high resolution XTEM and SAED (STEM, Inc.). This film was also determined to be

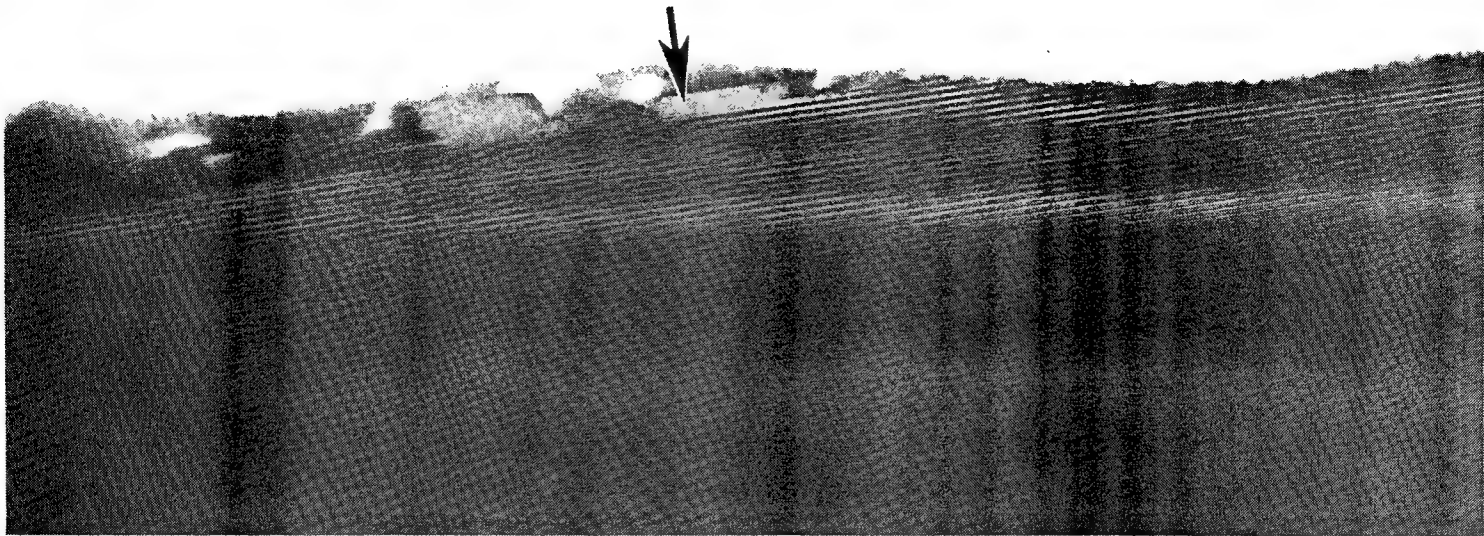


Figure 14. Cross-Section TEM Image of the 3C-SiC/6H-SiC Interface Showing Continuity of the Substrate Lattice Fringes into the 3C-SiC Film (arrow). Magnification 660,000 X. The Film was Grown at 1175°C on a 6H-SiC (0001) Substrate.

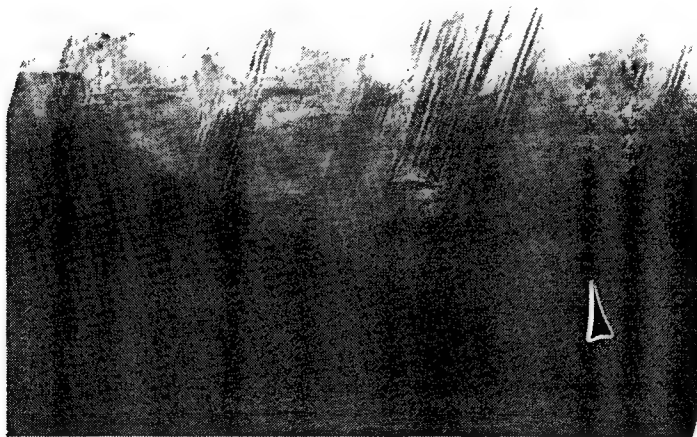


Figure 15. Cross-Section TEM Image of the 3C-SiC Film. Fringes of the (0006) Planes of the 6H-SiC Substrate are Faintly Seen (arrow).

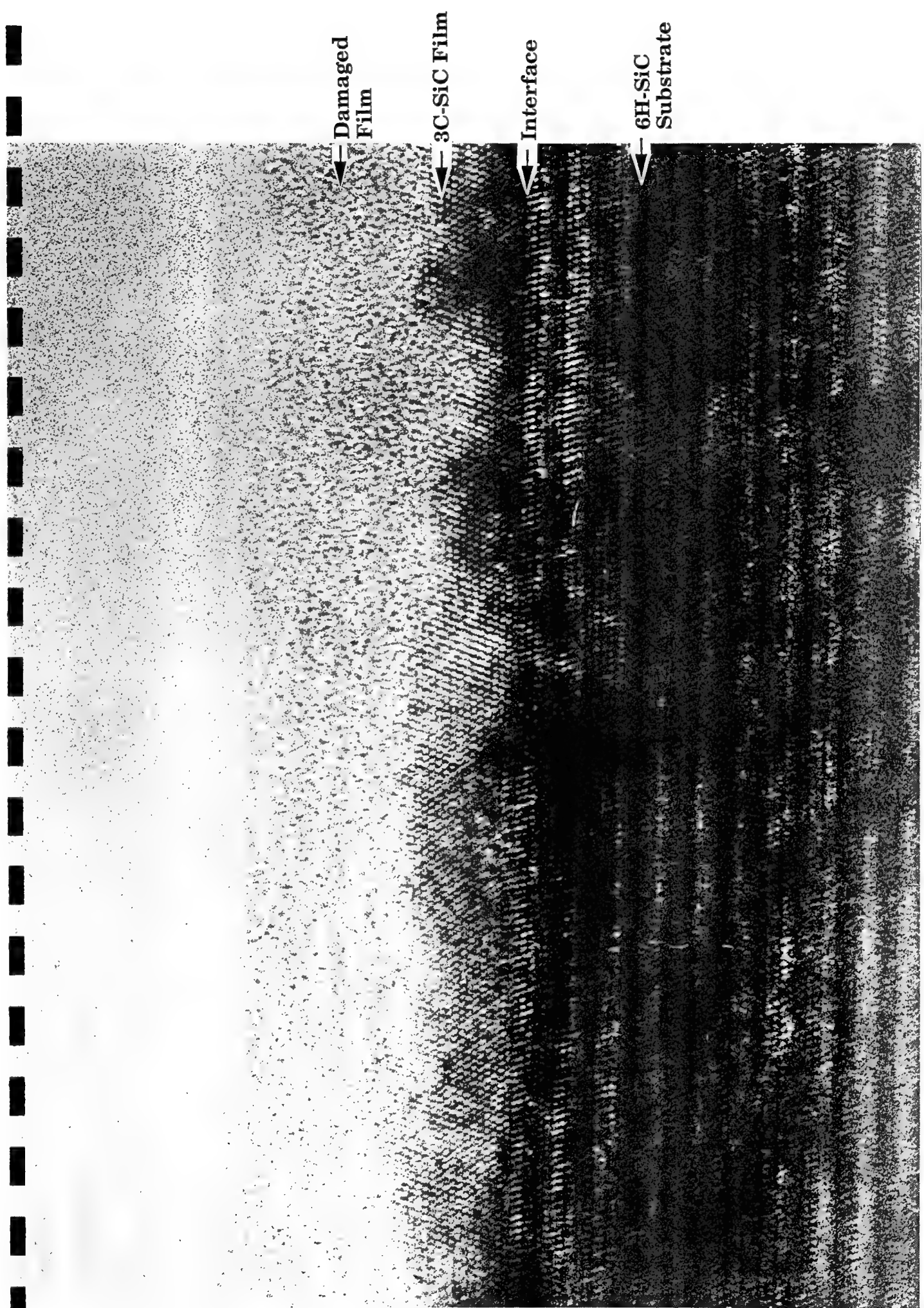


Figure 16. Atomic Resolution TEM Image of the 3C-SiC Film/6H-SiC (0001). Interface Magnification = 5,730,000 X. The Interface is Atomically Smooth.

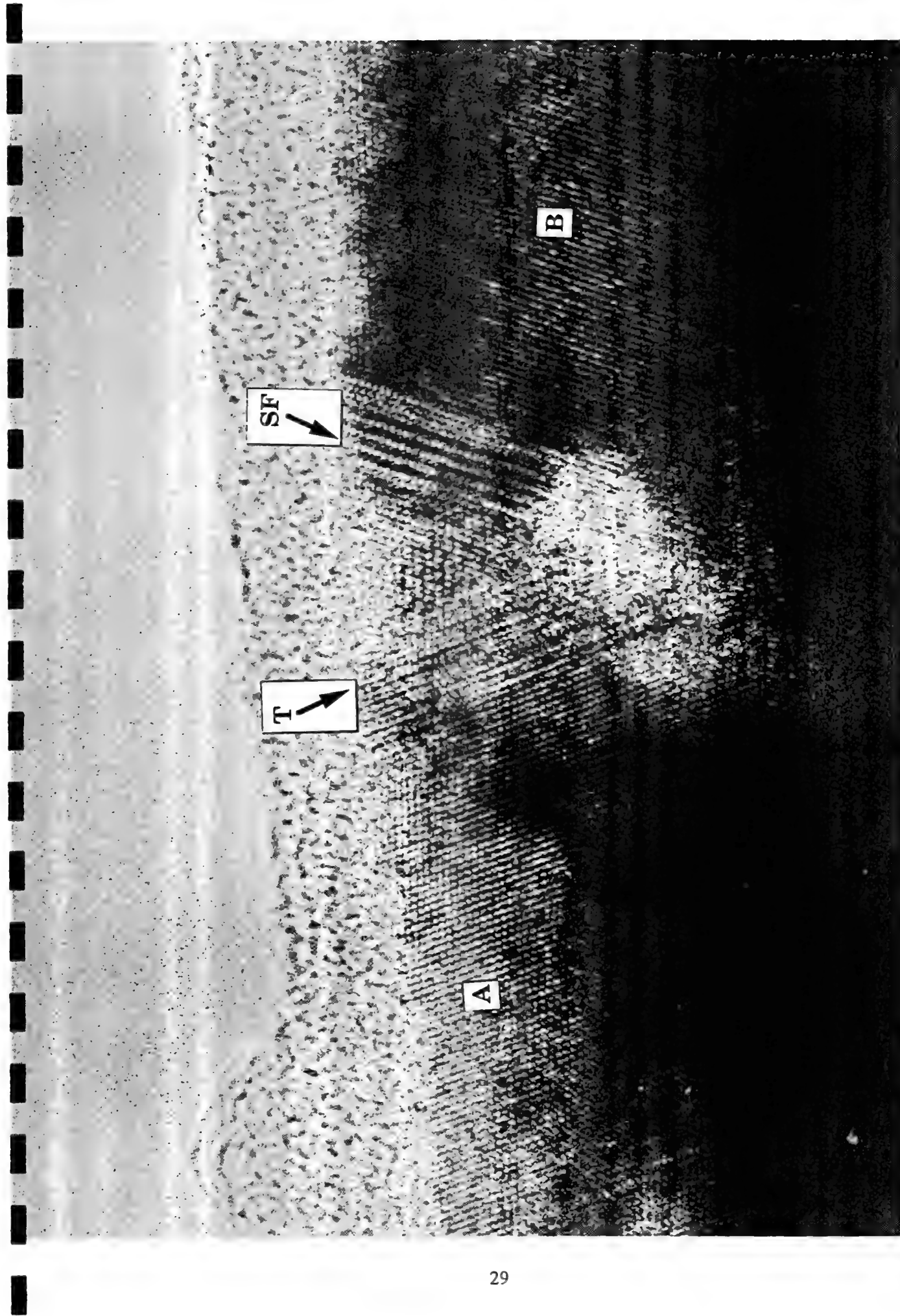


Figure 17. Atomic Resolution TEM Image of the 3C-SiC Film Showing Double Positioning of Regions A and B. Stacking Faults (SF) and Twins (T) are Observed at the Junction of the Two Domains.

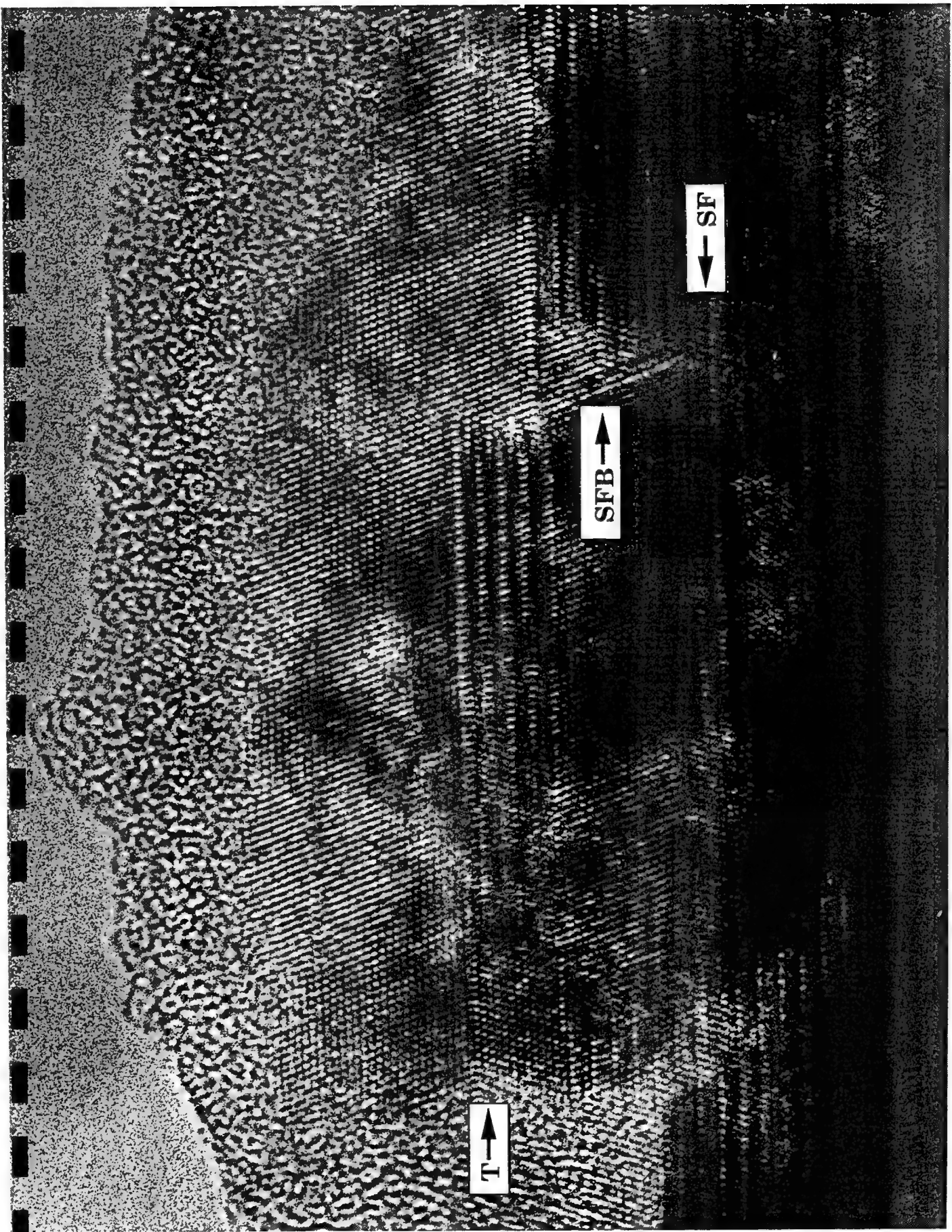


Figure 18. Atomic Resolution TEM Image of the 3C-SiC Film Revealing a Twin (T) Parallel to the 6H-SiC (0001) Substrate. Also Shown is a Stacking Fault Boundary (SFB) which Occurs from Fault in the 3C Stacking Sequence (SF).

single crystal 3C-SiC (111) with stacking faults and twins. Figure 19 depicts an electron diffraction pattern obtained at the film/substrate interface along with a schematic illustration of the indexed pattern. As with the sample described above, the pattern reveals the exact superposition of the 6H-SiC $[11\bar{2}0]$ and 3C-SiC $[110]$ such that the (0001) substrate plane is parallel to the (111) film plane. The pattern also shows the superposition of a third pattern which is the twin orientation of 3C-SiC $[110]$. When a 3C $[110]$ twins, the twin orientation is also a $[110]$ except that the pattern is reflected about the (111) twin plane. Streaking along two directions is also observed. The streaking is believed to occur because of, 1) twins in the matrix and, 2) twins with twins. These observations are schematically illustrated in Figure 19.

Figure 20 depicts a high resolution TEM image of the interface that demonstrates that the lattice planes in the film are parallel to those in the substrate. This observation provides evidence that the 3C-SiC phase is formed epitaxially on the 6H-SiC substrate. The image also shows a high density of twins which is consistent with the electron diffraction data. Also note the steps on the substrate surface which are formed when polished 3.5° towards $[11\bar{2}0]$.

FT-IR Results - The SiC film properties were assessed by Fourier transform infrared (FT-IR) measurements. The methods are adaptable to in-situ monitoring of the growth process as well as for ex-situ film characterization. In Phase I, through routine ex-situ measurements performed on each film, we determined that the infrared reflectance of the films varied greatly with sample quality and deposition conditions. Theoretical analysis based on a detailed physical model of the SiC dielectric function yielded quantitative information on the properties of the films.

In Figure 21 we compare the measured infrared reflectance spectra of films grown on Si at 930°C at 4 different laser fluences. The reflectance spectrum of SiC thin films is dominated by a strong peak around 800 wavenumbers. This peak is called the restrahlen peak, and is due to a long wavelength transverse optical (TO) phonon mode. The width, position and amplitude of this peak are sensitive to disorder, porosity, stress, thickness and doping in the film. A dip at $\sim 870\text{ cm}^{-1}$ is due to the Longitudinal Optical (LO) phonon mode. Detailed physical modeling (discussed below) can be used to extract information about these film qualities, however, a simple qualitative examination of the reflectance will also yield useful information about the film quality. Note in Figure 21 that the restrahlen peak becomes increasingly narrow as the laser fluence is decreased from 14 J/cm^2 to 1.5 J/cm^2 . This indicates that the TO resonance is becoming increasingly narrower, a signature of higher quality crystalline material. The crystalline quality of these films as determined by XRD (discussed earlier) correlated well with this observation.

In Figure 22 we compare the measured infrared reflectance of three films grown on Si at different temperatures. These films were all of the same nominal thickness (150 nm), and were deposited at the same fluence of 1.5 J/cm^2 . The strength of the TO reflection resonance was clearly highest for the film grown at the highest temperature. Again, the XRD data discussed previously confirmed that the films crystallinity improved with increasing temperature.

The reflectance of a silicon carbide thin film was calculated using the matrix method of Abeles (30). The optical properties of the SiC were computed using a simple model (developed under this program) for the infrared dielectric function:

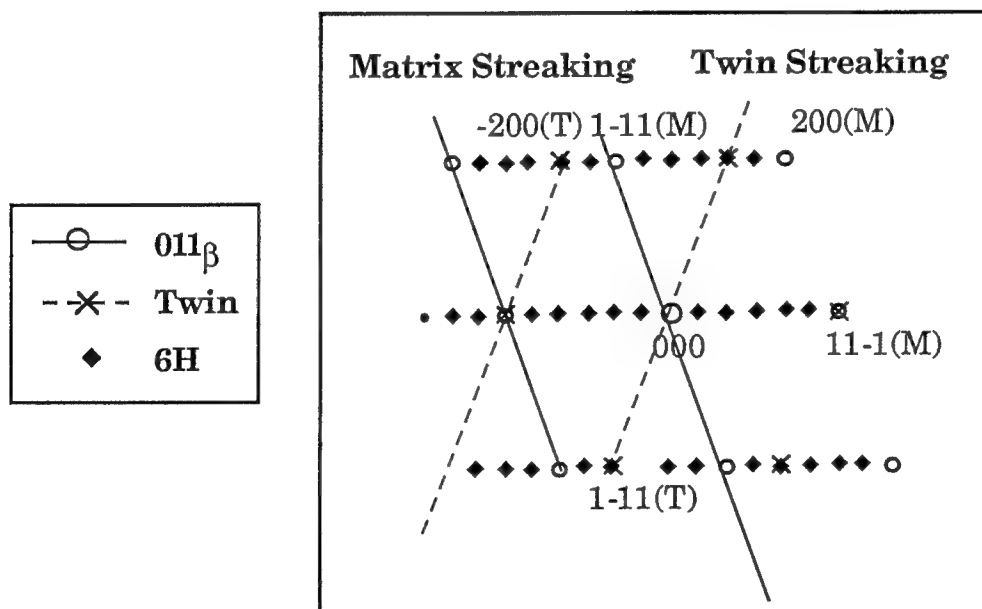
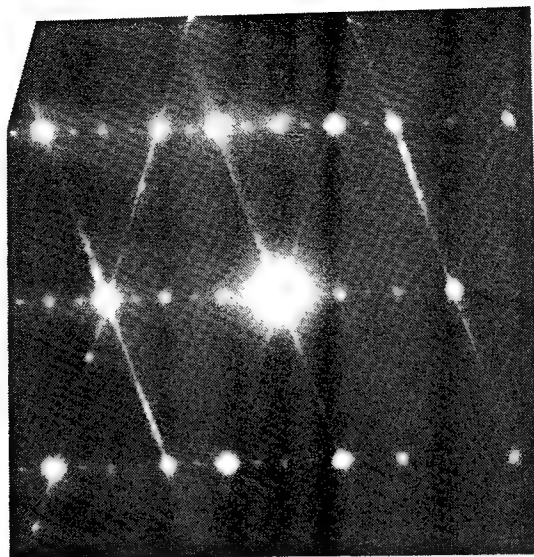


Figure 19. SAED Pattern and Schematic Illustration of the Film/Substrate Interface of a SiC Film Grown on a Vicinal 6H-SiC (0001) Substrate Oriented 3.5° Towards $[11\bar{2}0]$ at 1200°C . The Pattern Reveals the Perfect Superposition of the 6H-SiC $[11\bar{2}0]$ and 3C-SiC $[110]$. The Pattern also Shows a Third Orientation Which is the Twin Orientation of $[110]$. One Set of Streaks is Due to Twins in the Matrix and the Other is Due to Twins Within the Twins.



Figure 20. Cross-Section TEM Image of the 3C-SiC/6H-SiC Interface of Vicinal 6H-SiC (001) Substrate. The Lattice Fringes of both the Substrate and Film are Clearly Observed. Magnification = 2,200,000 X.

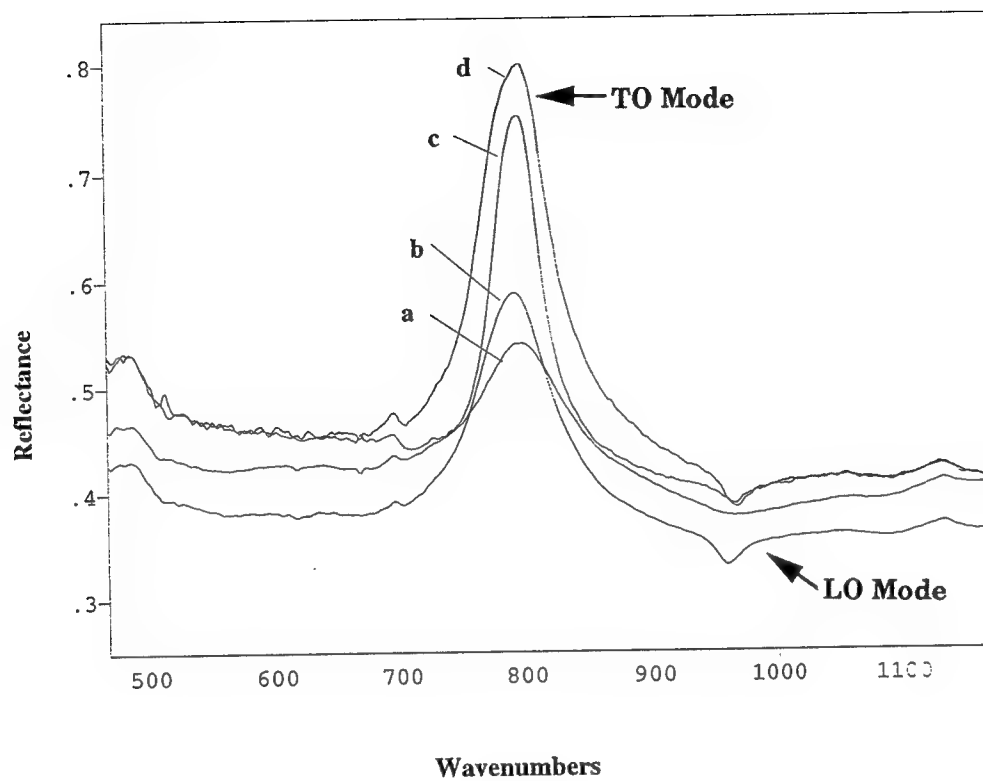


Figure 21. Infrared Reflectance Spectra of SiC Films Grown on Si (100) at Fluences of a) 14 J/cm^2 ; b) 7 J/cm^2 ; c) 1.5 J/cm^2 ; and d) 2.8 J/cm^2 .

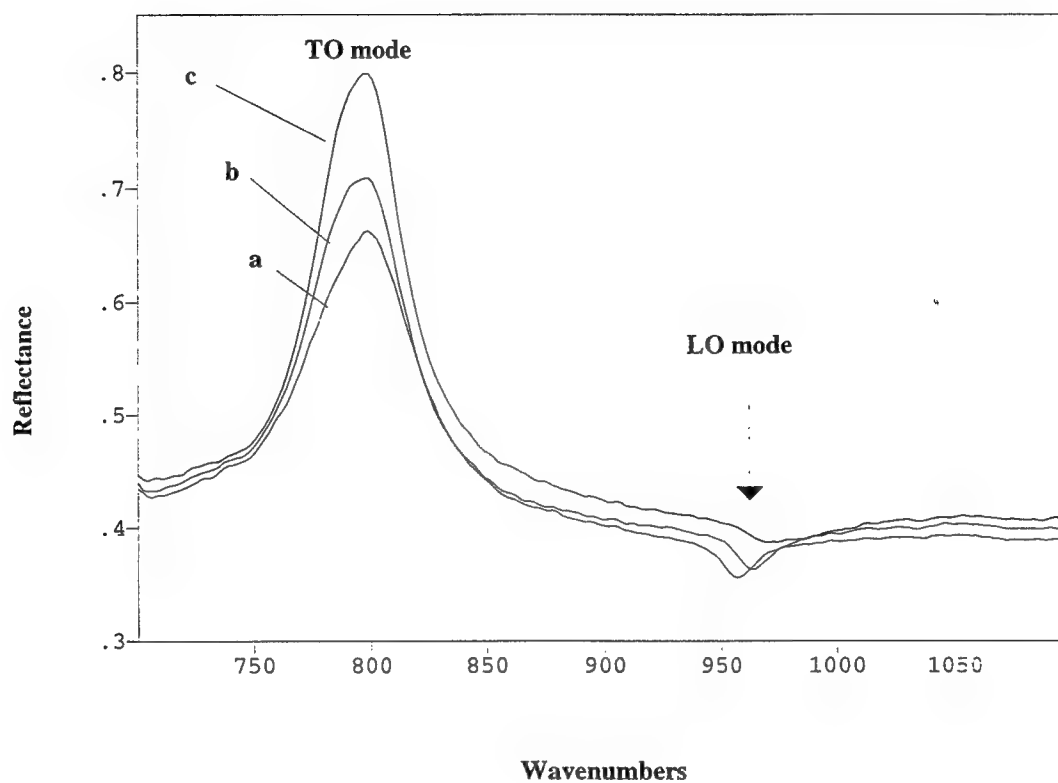


Figure 22. Reflectance Spectra Measured for Silicon Carbide Films Grown at: a) 857°C; b) 935°C; and c) 1055°C.

$$\varepsilon(\nu) = \varepsilon_{\infty} - \frac{4\pi ne^2}{\nu^2 + i\nu\gamma_{fc}} + \frac{\nu_p^2}{\nu_{TO}^2 - \nu^2 - i\nu\gamma_{TO}} \quad (1)$$

Where n , m^* and γ_{fc} represent the density, effectiveness and scattering rate of the free carriers, and ν_p and γ_{TO} represent the plasma frequency and scattering rate of the TO phonon mode, respectively. In Eq. (1), the first term represents the high frequency (visible or near IR) dielectric constant (~ 6.7 for high quality bulk SiC). The second term represents the Drude contribution of the free carriers. The third term represents the Lorentzian contribution of the dominant TO phonon mode of the SiC crystal lattice.

Given this model for the dielectric function, and an analogous one for the substrate, we calculate theoretical reflectance spectra, based on sets of values for the sample dependent parameters such as $n, \varepsilon_{\infty}, \gamma_{fc}, \nu_p, \nu_{TO}$, and γ_{TO} and the film thickness. By comparing the simulated spectrum to the measured spectrum and adjusting the free parameters to best fit the measured spectrum, we extracted the fundamental materials properties defining the model in Eq. 1. This procedure allowed the determination of the film thickness and electronic properties from the infrared reflectance.

Figure 23 shows the results of fitting the theoretically model reflectance to a measured spectrum for a SiC film grown at $2\text{J}/\text{cm}^2$. The model parameters for the film were varied to best match the theoretical curve to the measured spectrum. The agreement between the model fit and the measured spectrum are excellent over most of the spectral range. The small deviations between the fit and the measurement are artifacts of a spurious reflection from the sample holder. The fit yielded a film thickness of 1500 \AA , in good agreement with an independent measurement of 1574 \AA by RBS. The parameters of the fit, as well as some literature values for the parameters are shown in Table 1.

| Model parameter | Fit results | Literature values for bulk material |
|------------------------|------------------------|-------------------------------------|
| ε_{∞} | 5.9 | 6.7 |
| ν_p | 1340 cm^{-1} | 1442 cm^{-1} |
| ν_{TO} | 794 | 793 cm^{-1} |
| γ_{TO} | 20 | 4.76 |

Table 1. Fitting parameters extracted from fitting the reflection spectrum predicted using Eq. 1 to a measured spectrum.

The measured TO frequency ν_{TO} agrees very well with literature values. This attests to the high quality of the SiC material within the film. The high phonon scattering rate γ_{TO} and the low value for ε_{∞} suggest that there are minority phase inclusions or porosity within the film. The plasma frequency (ν_p) is related to the density of bonds by $\nu_p^2 = 4\pi Nq^2 / m_{red}$, where N is the bond density, q is the ionic charge and m_{red} is the reduced mass. From our measurement of the ν_p we obtain that the SiC is effectively 86% dense. This corresponds well with the ratio of the measured value of ε_{∞} to the literature value. This is quite reasonable because both parameters depend in a similar way on the bond density of the material. The RBS analysis for this film yielded an excess carbon concentration of 13%. We attribute the deviations of the dielectric constant, phonon scattering rates and plasma frequencies to inclusions of

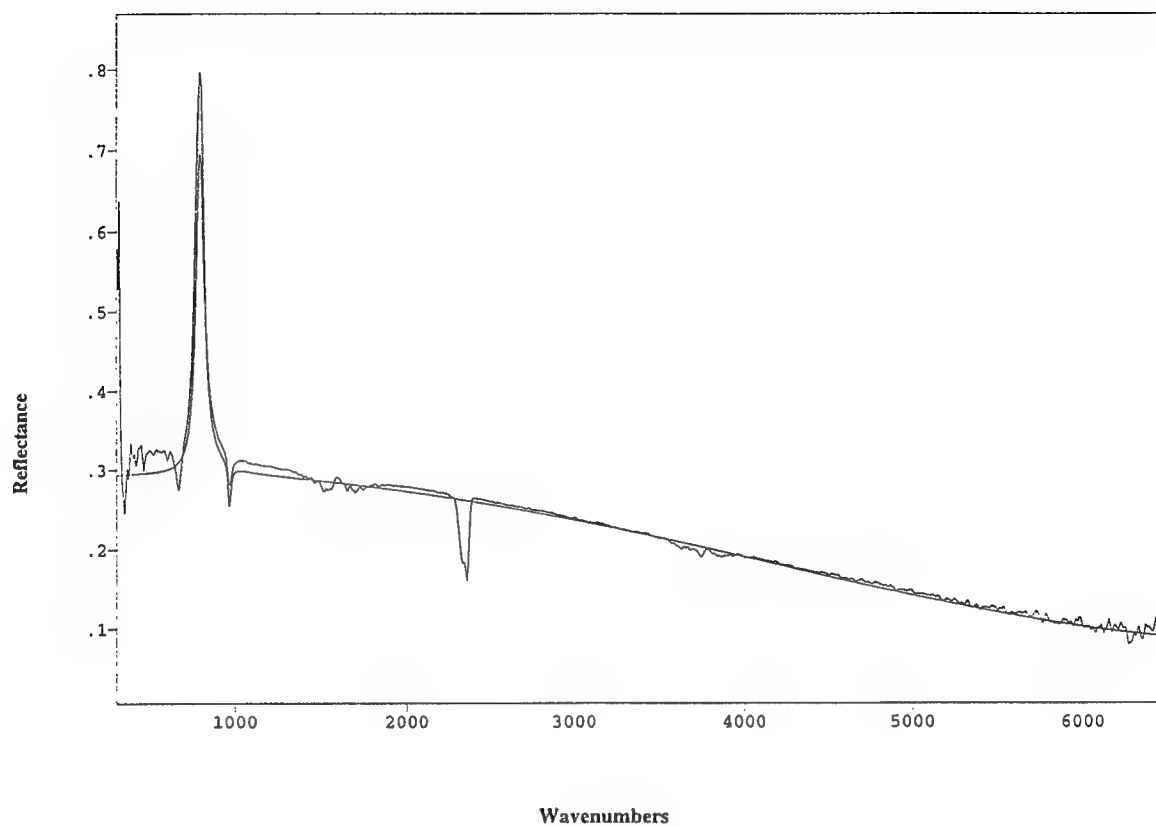


Figure 23. Comparison of Theoretical Fit and Measured Reflectance Spectrum of a SiC Film Grown on Si(100).

excess carbon. This point of view is further justified by the observation, that of the model parameters listed above, v_{TO} should not be strongly sensitive to the effects of impurity phases and porosity.

Electrical Characterization - Electrical characterization of the SiC films is important because the primary interest for SiC thin films is for electronic applications. In Phase I, current-voltage (I-V) measurements were attempted on SiC films grown on both Si (100) and 6H-SiC (0001) substrates. The leakage current and ideality factor can be obtained by the measuring the I-V characteristics in both directions. Large leakage currents have been associated with stacking faults, DPB's and other crystallographic defects. Au contacts were evaporated onto the SiC films. I-V measurements were obtained using a Keithley model 224 programmable constant current source, a Fluke model 8842 A programmable digital voltmeter, and a PAR model 5210 programmable lock-in amplifier. The measurements were controlled and recorded via a PC-386 computer. The films displayed low resistances (less than $1\text{ k } \Omega$) and ohmic behavior. We believe that the carbon contamination (described above) was responsible for the high conductivity of these films. Because the carbon contamination problem could not be overcome in Phase I, no further electrical measurements were performed.

Acknowledgements

The authors gratefully acknowledge the financial support of this research by the Small Business Innovation Research program of the U.S. Air Force (Contract No. F33615-94-C-5417). The authors also thank Dr. Mike Capano at Wright-Patterson AFB for his assistance in performing some of the x-ray diffraction measurements.

References

1. Edgar, J.H., *J. Mater. Res.*, **7**, 235, (1992).
2. Davis, R.F. and Glass, J.T., Advances in Solid State Chemistry, JAI Press, Ltd., (1991).
3. Golecki, I., Reidinger, F., and Marti, J., *Appl. Phys. Lett.*, **60**, 1703, (1992).
4. Molnar, B., *J. Mater. Res.*, **7**, 2465, (1992).
5. Powell, J.A., Larkin, D.J., Matus, L.G., Choyke, W.J., Bradshaw, J.L., Henderson, L., Yoganathan, M., Yang, J., and Pirouz, P., *Appl. Phys. Lett.*, **56**, 1352, (1990).
6. Morkoc, H., Strite, S., Gao, G.B., Lin, M.E., Sverdlov, B., and Burns, M., *J. Appl. Phys.*, **76**, 1363, (1994).
7. Fenner, D.B., Biegelson, D.K., and Bringans, R.D., *J. Appl. Phys.*, **66**, 419, (1989).
8. Fenner, D.B., Biegelson, D.K., Bringans, R.D. and Krusor, B.S., Materials Research Society Symposium Proceedings "Chemistry and Defects in Semiconductor Heterostructures," (Eds., M. Kawabe, E.R. Weber, T.D. Sands, and R.S. Williams), Materials Research Society, Pittsburgh, PA, 279, (1989).
9. Fork, D.K., Fenner, D.B., Barton, R.W., Phillips, J.M., Connell, G.A.N., Boyce, J.B., and Geballe, T.H., *Appl. Phys. Lett.* **57**, 1161, (1990).
10. Fork, D.K., Fenner, D.B., Connell, G.A.N., Phillips, J.M., and Geballe, T.H., *Appl. Phys. Lett.*, **57**, 1137, (1990).
11. Morrison, P.W., Jr., Cosgrove, J.E., Fenner, D.B., and Li, Q., "Epitaxial Growth of Single Crystal Diamond on Silicon," Final Report for U.S. Department of Defense SDIO, Contract No. N00014-91-C-0101, (1991).
12. Fenner, D.B., Li, Q., Morrison, P.W., Jr., Cosgrove, J.E., Lynds, L., and Johansson, M.E., "Pulsed Laser Deposition of CdTe, HgCdTe, and β -SiC Thin Films on Silicon," Spring MRS Meeting, (1992).
13. Nishino, S., Powell, J.A., and Will, H.A., *Appl. Phys. Lett.*, **42**, 460, (1983).
14. Kong, H.S., Wang, Y.C., Glass, J.T., and Davis, R.F., *J. Mater. Res.*, **3**, 521, (1988).
15. Wahab, Q., Sardela, M.R., Jr., Hultman, L., Henry, A., Willander, M., Janzen, E., and Sundgren, J.E., *Appl. Phys. Lett.*, **65**, 725, (1994).
16. Kong, H.S., Kim, H.J., Edmond, J.A., Palmour, J.W., Ryu, J., Carter, C.H., Jr., Glass, J.T., and Davis, R.F., (Eds. In Aselage, T., Emin, E., and Wood, C.), *Mater. Res. Soc. Sym. Proc.*, Materials Research Society, Pittsburgh, PA, **97**, 233, (1987).
17. Stan, M.A., Patton, M.O., Warner, J.D., Yang, J.W., and Pirouz, P., *Appl. Phys. Lett.* **64**, 2667, (1994).
18. Rowland, L.B., Kern, R.S., Tanaka, S., and Davis, R.F., *J. Mater. Res.*, **8**, 2753, (1993).
19. Yoshinobu, T., Mitsui, H., Izumikawa, I., Fuyuki, T., and Matsunami, H., *Appl. Phys. Lett.*, **60**, 824, (1992).
20. Nishino, K., Kimoto, T., and Matsunami, H., "Proc. Fifth Silicon Carbide and Related Materials Conf.," (Ed., M.G., Spencer), **137**, 33, (1993).
21. Yoo, W.S., Hamaguchi, N., Carulli, J.M., Jr., Buchan, N.I., Tischler, M.A., Chien, F., and Nutt, S.R., "Proc. Fifth Silicon Carbide and Related Materials Conf.," (Ed. M.G. Spencer), **137**, 259, (1993).
22. Hubler, G.K., Pulsed Laser Deposition of Thin Films, (Eds. D.B. Chrisey, and G.K. Hubler), 327, (1994).
23. Donley, M.S., and Zabinski, J.S., Pulsed Laser Deposition of Thin Films, (Eds. D.B. Chrisey and G.K. Hubler), 431, (1994).

24. Chen, L., Pulsed Laser Deposition of Thin Films, (Eds. D.B. Chrisey and G.K. Hubler), 167, (1994).
25. Greer, J.A., Pulsed Laser Deposition of Thin Films, (Eds. D.B. Chrisey and G.K. Hubler) 293, (1994).
26. Greer, J.A. and Tabat, M.D., Paper Presented at the 41st National Symposium on the AVS, Denver, CO, (Oct. 1994).
27. Peters, L., Semiconductor International, p. 56, (Aug. 1991).
28. Markham, J.R., Kinsella, K., Carangelo, R.M., Brouillette, C.R., Carangelo, M.D., Best, P.E., and Solomon, P.R., Rev. of Sci. Instr., **64**, 2515, (1993).
29. Chiu, C.C., and Deso, S.B., J. Mater. Res., **8**, 535, (1993).
30. Hecht and Zajac, "Optics", Addison-Wesley Publishing Co. 1979